THE

Chemical Significance
of Optical Dispersion

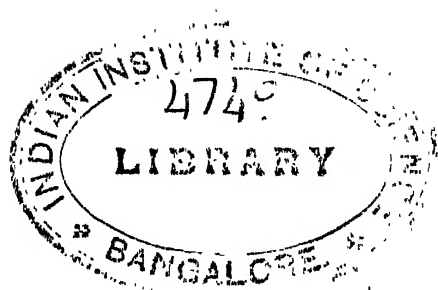□ □ □

A THESIS
SUBMITTED TO THE
UNIVERSITY OF LONDON
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DOCTOR OF SCIENCE

BY

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PREFACE

THIS dissertation summarises the experience of the writer during the six years in which he has been engaged on this work, first as research assistant to R. H. Pickard, D.Sc. (Lond.), F.R.S., F.I.C., and later as lecturer in Physical Chemistry and Chemical Engineering in the Chemical Department of the Battersea Polytechnic under the direction of J. Kenyon, D.Sc. (Lond.), F.I.C. To both these gentlemen he desires to offer his sincere thanks for their cordial advice and helpful criticism. His best thanks are also due to Miss E. Osbaldiston, B.Sc. (Lond.), for reading the MS. and offering many valuable suggestions as to its form.
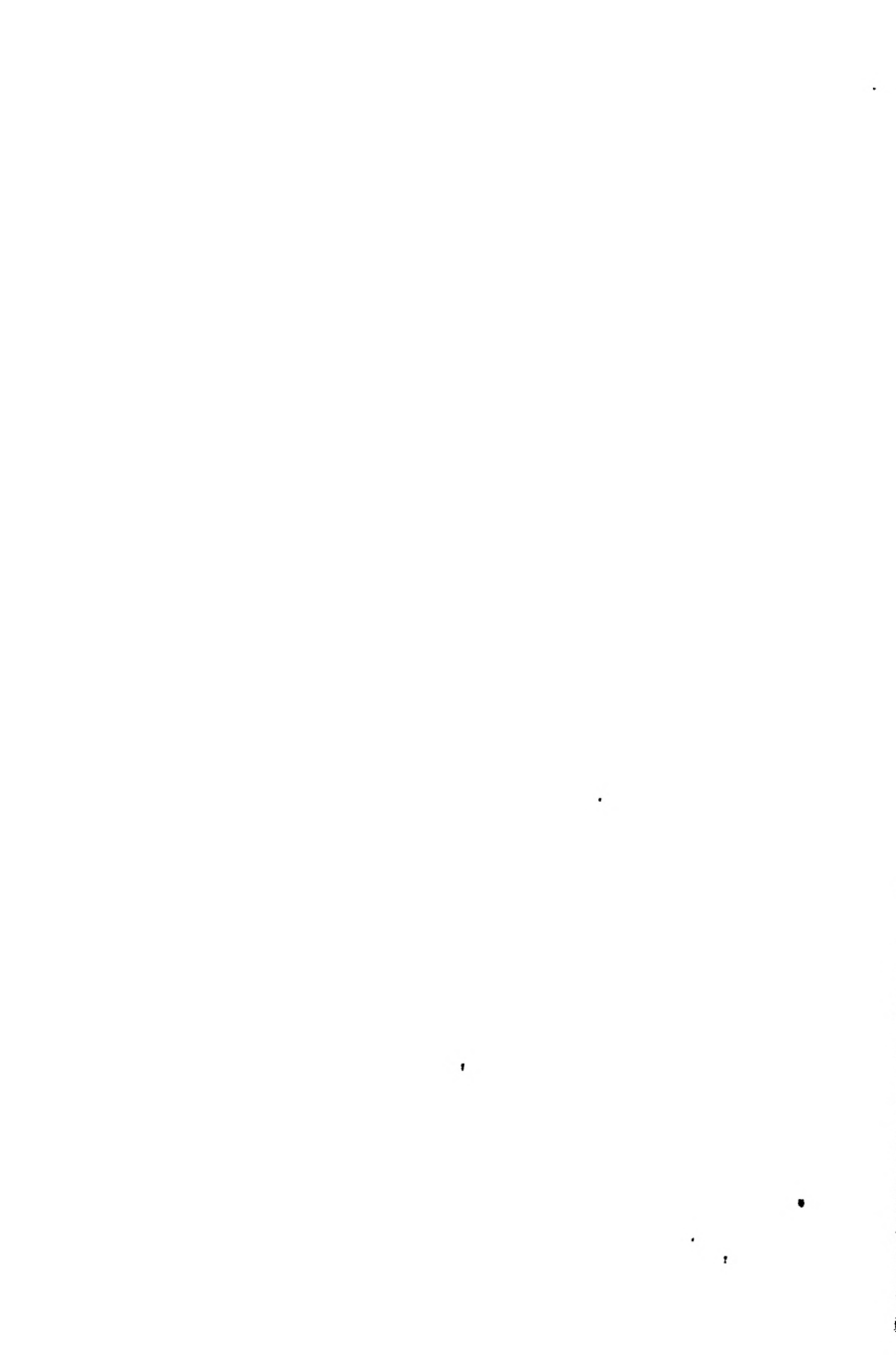
The thesis is intended to supply an extended and critical survey of the whole subject and is primarily designed to meet the needs of young graduates who are making their first acquaintance with the methods of research in the laboratories of the Battersea Polytechnic. The writer's contributions to the literature of the subject have all been communicated to the Chemical Society of London, in his own name and conjointly.

CONTENTS.

The Chemical Significance of Optical Dispersion.

I.

INTRODUCTORY.

The optical properties of a material medium depend for their numerical value on the wave length of the light used in determining them. This effect is known as " optical dispersion," and it is at once obvious that no investigation of the dependence of optical properties on chemical constitution can be considered complete unless the effect of dispersion be taken into account. Indeed, it may even prove to be impossible to study the effect of chemical constitution on some optical property until dispersion effects have been thoroughly studied with a view to their elimination. For a clear understanding of the effect of dispersion on an optical property, it is imperative to know exactly —or at least as exactly as experimental methods will permit—the manner in which the numerical value of the property varies with the wave length of the light. Therefore measurements must not be confined to those with light of one wave length only, nor is it sufficient for this purpose to measure dispersion as the difference in the values, or as a ratio of the values, of the particular property for light of two arbitrarily chosen wave lengths. The actual form of the function connecting the two variables must, if possible, be determined. This fundamental condition for successful investigation was clearly understood by the earlier workers in this field, but has been more or less completely ignored, until recent years, by their successors.

In the following pages it is proposed to deal with the effect of dispersion on the three optical properties, natural rotatory power, refractive index and magnetic rotatory power, and, as the connection between these properties (considered in the main without reference to the effect of dispersion) and chemical constitution has been treated

very fully in many text-books and monographs, only such reference to this connection will be made as is necessary to the logical development of the thesis.

Before proceeding to the consideration of each of these three properties in detail, it will, perhaps, be well to consider a few of the practical points involved. The problem of the light source is probably the most important of these. The obvious course for any investigation of dispersion to take is either :—

(a) the proposal of a dispersion equation, followed by an attempt to verify it experimentally, or

(b) the accumulation of experimental figures, followed by an attempt to obtain a formula to fit them.

In either case it will be necessary to obtain measurements of the numerical value of the particular property under consideration for monochromatic light of known wave length. Three methods of securing such monochromatic illumination present themselves :—

(i.) a source of light emitting a continuous spectrum may be used and suitable bands which are approximately monochromatic may be isolated by means of light filters,

(ii.) a source of light emitting a continuous spectrum may be used and suitable bands which are very nearly monochromatic may be isolated by means of a spectrometer and a subsidiary light source which is a true monochromat but which for some reason—feeble intensity or evanescent character—is unsuitable for direct use,

(iii.) a source of light emitting a discontinuous spectrum may be used, the beam being spectroscopically resolved at some point in its path so that measurements can be made with the truly monochromatic individual lines.

Of these methods (i.) has been widely employed[1] by workers in the past, but it is not a good one because the bands are by no means monochromatic—all light filters exhibit relatively broad transmission bands—and the method is useless for measurements with any claim to precision. Method (ii.) has been employed[2] particularly for polarimetric work. Its advantage lies in the fact that a very intense source of light, for example a Nernst or Pointolite lamp, may be employed, thus increasing the ease with which measurements can be made and therefore presumably increasing their accuracy. It suffers, however, although to a less extent, from the same disadvantage as the first

method ; it does not provide truly monochromatic illumination and can not be used in polarimetric work with bodies possessing high rotatory power.

The most scientific method of illumination is undoubtedly the third, but hitherto the feeble intensity of some of the available sources has prevented its more general adoption. For polarimetric work especially, it is essential to employ an intense illuminant, as the following considerations will show. By the total internal reflection of the ordinary ray in the polarising Nicol, 50 per cent. of the incident light is rejected. When the analysing Nicol is set to extinction a fraction of the remaining 50 per cent. equal to the cosine of half the half-shadow angle is again rejected. Finally, there is, in addition, loss of light by reflection from the surfaces and absorption in the material of the optical parts of the polarimeter. Flames and vacuum tubes are generally quite suitable for refractometric measurements, but the only really satisfactory flames for use with the polarimeter are those of sodium and lithium vapour, whilst vacuum tubes are far too feeble for use with this instrument. We are thus forced to rely on open and enclosed arcs as sources of light. Fortunately, the enclosed mercury arc is a commercial article which furnishes a spectrum consisting essentially of an intense yellow doublet, an intense green and a strong violet line. Should the similar enclosed cadmium arc[3] ever become a practical success, it will undoubtedly become even more useful than the mercury arc because it affords four brilliant lines of exceptional purity, one red, one green, and two blue. These two arcs—with perhaps the sodium and lithium flames included—thus cover the whole of the visible spectrum in a very satisfactory way[4] and, in addition, possess the very great advantage of requiring only a direct-vision spectroscopic eyepiece for resolution of their spectra. Open arcs, though equally intense, suffer from several disadvantages ; they seldom burn steadily, they generally require a hood to remove noxious fumes, and their spectra are always so complex as to require special apparatus to purify the light before it enters the polarimeter. Arcs of this type between electrodes of copper, brass (copper-zinc), and silver-cadmium are the ones most frequently employed.

The experimental determination of the form of any dispersion curve, whether it be rotatory or refractive, is rendered exceedingly difficult by the fact that the visible and hence easily accessible portion of the electromagnetic spectrum forms such a small fraction of the whole. The investigations of physicists have now made us acquainted

with what is practically a continuous spectrum extending from the very short waves (10^{-9} cm.), γ-rays, emitted from radioactive bodies, to the very long Hertzian " wireless " waves with a length of 10^9 cm., a compass of about sixty octaves. Of this large compass, the visible spectrum forms slightly less than one octave—from 4×10^{-5} cm. to $7 \cdot 5 \times 10^{-5}$ cm. The necessity for careful deduction and guarded statements is therefore obvious ; what is apparently true in the visible region of the spectrum may be very far from the truth when measurements are pushed into some previously unexplored region. Fortunately, a method is available by which observations of refractive index and of rotatory power may be extended into the ultraviolet region of the spectrum as far as radiations of wave length $2 \cdot 5 \times 10^{-5}$ cm. and it may prove possible to explore the infra-red region as far as $1 \cdot 5 \times 10^{-4}$ cm. in a similar manner. This method is a photographic one, and is already yielding very interesting results in at least three laboratories in this country. It is probable that the lower ultraviolet limit indicated above will prove impassable for some time to come for reasons connected with the opacity of the materials used in the optical parts of our measuring instruments. Measurements of refractive index have, however, been made with radiations of wave length 9×10^{-4} cm. and there seems to be no valid reason why polarimetric measurements should not ultimately be carried out in this infra-red region of the spectrum, possibly by means of a bolometer or other delicate heat measuring instrument.

It must be remembered, too, that the radiation-absorbing properties of the bodies under examination may introduce experimental difficulties into the work. Optical investigation over extended regions of the electromagnetic spectrum has been successful only in very few cases, and has been confined exclusively to naturally occurring crystals of great transparency. Research on these lines has been carried out almost entirely by physicists and has been directed mainly to physical ends. Compounds of theoretical interest to the chemist are, in general, relatively opaque. They mostly exhibit absorption bands in the near infra-red and are rarely as transparent in the ultraviolet as quartz or the other crystals found in nature.

Another point which must not be lost sight of is the relative crudity of the polarimeter as an instrument for quantitative work. In addition to the difficulties of construction common to all optical instruments of precision—the correct design, achromatisation and assembly of the lens system, the accurate centering and graduation of the divided

circle carrying the analyser—it suffers from drawbacks which are peculiarly its own. The necessity for purity of light source, which has already been pointed out, is possibly the least of these. Another drawback lies in the fact that polarimetric measurements are made when the light reaching the eyepiece is of necessity at its dimmest. The setting of the instrument depends on the matching of two shades of a colour of very low intensity, so that an error of no inconsiderable magnitude due to personal equation may be introduced into the measurements.

An attempt is being made in these laboratories to get over this difficulty by using the photo-electric properties of the element selenium. This substance has a specific resistance which is diminished on exposure to light, so that it may be employed for photometric purposes. Briefly, the idea underlying the method is to use a small selenium cell connected in series with a suitable source of E. M. F. and a sensitive galvanometer and to adjust the setting of the polarimeter until no change of the galvanometer deflection occurs when the cell is moved from one half of the polarimeter field to the other. The method is adapted from that described by TOY and RAWLING[5] for measuring the density of the image on a photographic plate, and is being applied to polarimetric work by Miss DICKES.. There are several difficulties yet to be overcome. First, the illumination of the polarimeter field is of such low intensity that the resistance of the necessarily small selenium cell is very high. One of the cells at present in use has a " dark " resistance of 180,000 ohms. The second important difficulty is that selenium appears to be much less sensitive to polarised light than to non-polarised light. The remedy appears to be either to resort to amplification by means of a triode valve or else to depolarise the light after it leaves the polarimeter.

II.

NATURAL ROTATORY POWER.

Substances which possess the property of rotating the plane of polarisation of a beam of plane polarised light are said to be " optically active " or to exhibit the phenomenon of " rotatory polarisation." More than a century has passed since the phenomenon of optical activity was first observed by ARAGO[6] in 1811 in the case of quartz, by BIOT[7] in 1815 in the case of organic compounds, and by FARADAY[8] in 1846 in the case of substances subjected to the influence of a magnetic field. In spite of the lapse of time, however, and of the vast amount of work that has been done on the subject, there is to-day only one fact which has been established with sufficient certainty to acquire the standing of a scientific law. This fundamental law is that optical activity is always associated with asymmetry. All optically active substances exist in enantiomorphous forms. The converse of this statement is, however, not true. Substances are known which exist in enantiomorphous forms, and yet are not optically active. So far examples of this latter phenomenon have been found only among crystals, of which ammonium chloride, lithium sulphate monohydrate and nickel sulphate hexahydrate are examples. In view of this fact, then, it is not justifiable to assume that failure to resolve compounds possessing an asymmetric molecular structure into optically active forms is due to the lack of experimental methods of sufficient power. It may be—in fact, it has already been suggested[9]—that something more than enantiomorphism of structure is necessary to produce optical activity, or, alternatively, that enantiomorphism and optical activity are both manifestations of one fundamental cause and that the former may exist without the latter, but that whenever optical activity exists it is necessarily accompanied by asymmetry.

The asymmetry which determines optical activity may be classified conveniently under two heads :—

(i.) asymmetry of condition,
(ii.) asymmetry of form.

In the first-class falls magnetic rotatory power, in which the optical activity is due to the forces set up by the magnetic field as asymmetric agent. All bodies, so far as we know, exhibit magnetic rotation—iron, for example, rotates the plane of polarisation of a beam of sodium light through 4° for a layer 0·0002 mm. thick when placed in a strong magnetic field.[10] The activity disappears when the exciting field is removed.

Optical activity due to asymmetry of form may be further subdivided into two classes :—

(a)   activity due to asymmetry of crystal structure,
(b)   activity due to asymmetry of molecular structure.

Class (a) includes such substances as sodium chlorate, quartz, benzil and cinnabar. Quartz[11] has a rotation of 21°, and benzil[12] one of 25° per millimetre of thickness for the D line, whilst cinnabar[13] has a rotation per millimetre of 325° for red light. For substances of this class, the activity disappears when the crystal form is destroyed, for example, by fusion or solution. It may happen, however, that a substance shows optical activity in both the crystalline and the dissolved states. Tartaric acid is an example of this type. In such cases, both the crystal structure and the molecular structure are asymmetric—solution destroys the former, but not the latter.

Class (b) is the one which includes the substances dealt with in the following pages, and is, for the purpose of this thesis, restricted to those organic compounds containing a carbon atom directly linked to four different radicals. The optical activity of bodies in this class persists in the dissolved and vapour states.

The factors determining the magnitude of the angle of rotation observed in the polarimeter for any one substance are five in number :—

(a)   The length of tube or column of liquid through which the beam of polarised light has to pass. The angle of rotation is, *caeteris paribus*, directly proportional to this length.

(b)   The wave length of the light employed in the measurement. It is generally, but not invariably true that the rotation for light of short wave length is greater than that for light of longer wave length.

(c)   The temperature of the substance under observation. There is no general law : the temperature coefficient of rotation is sometimes small, sometimes large, sometimes positive and sometimes negative.

(*d*) The nature of the solvent—if any—employed. Here again, there is much confusion—no general law can be formulated, although a given solvent usually behaves with all optically active substances in the same general way. For example, carbon bisulphide is in general a depressing solvent. That is to say, solution in carbon bisulphide usually lowers the rotatory power of a substance, sometimes even to the extent of causing it to change sign. There are, however, exceptions to this rule, some optically active ethers, for instance, exhibiting increased rotatory power when dissolved in carbon bisulphide.[14]

(*e*) The concentration of solute in the solution. Generally speaking, dilution of an optically active solution, although it decreases the observed angle of rotation, increases the specific rotatory power.

It is thus apparent that the number of factors influencing the magnitude of the rotatory power of a compound is far too great to allow the detection of any simple, general, quantitative relations between chemical constitution and rotatory power unless precautions are taken either to eliminate some of them or to keep their influence constant throughout a series of investigations. This is where the majority of the earlier workers went wrong. They were trying to disentangle too many threads at once with the natural consequence that they were unable to interpret their results. The more obvious of their mistakes were :—

(*a*) The use of complex naturally occurring optically active substances, in most cases with no guarantee that they were fully resolved—*i.e.*, exhibiting their full rotatory power. These compounds, too, generally contained more than one asymmetric carbon atom, so that it was impossible to ascribe definite values to the effect of the separate asymmetric atoms.

(*b*) The use of solid compounds of which the rotatory power had to be determined in solution. The solvent effect was thus mixed up with the true rotatory power of the compound.

(*c*) The practice of recording the value of the rotatory power for light of one wave length only—the sodium D line was the one most generally favoured because it is cheaply

and easily produced. The effect of dispersion was thus completely ignored.

(d) Lastly, the earlier workers in this field rarely paid any attention to the effect of temperature on rotatory power.

This was roughly the position of the subject when, PICKARD and KENYON[15] devised, in 1907, a new and fairly general method for the resolution of alcohols into their optical isomerides. These investigators set themselves the task of discovering, if possible, some quantitative relationship amongst the rotatory powers of organic compounds. They cut themselves adrift from the old, stereotyped methods, commenced at the beginning, and worked on in a logical and scientific manner. Their method has been justified by its results, and is still being successfully applied. They planned an investigation of the rotatory powers of homologous series of secondary alcohols because these substances fulfilled the following requirements,[16] which these workers thought to be necessary for success :—

(i.) The compounds should possess a simple chemical structure.

(ii.) They should possess only one asymmetric carbon atom in the molecule.

(iii.) They should be liquid at the temperature of the laboratory or just above it in order that their rotatory powers may be determined in the homogeneous state without the necessity of employing solvents, the effect of which is indeterminate.

(iv.) The compounds should not all be derivatives of one parent optically active compound, thus minimising the danger of error if the parent compound should prove to be impure or incompletely resolved.

(v.) The compounds should be sufficiently non-volatile to enable the effect of temperature on rotatory power to be studied.

(vi.) The effect of substituents on the rotatory power should be compared only when these are directly attached to the asymmetric carbon atom.

Three such series were built up :—

(a) The " Methyl " series.[17] $CH_3 \cdot CH(OH) \cdot R$
where R is a normal saturated hydrocarbon radical and represents any of the groups from ethyl to n-undecyl.

(b) The " Ethyl " series.[18] $C_2H_5 \cdot CH(OH) \cdot R$
where R similarly extends from methyl to n-pentadecyl.

(c) The " *iso*Propyl " series.[19] $(CH_3)_2 C \cdot CH(OH) \cdot R$
where R extends from methyl to *n*-decyl.

These series were examined polarimetrically and the investigation was subsequently extended to include no less than fourteen homologous series of esters of these and similar alcohols with the normal saturated aliphatic monobasic acids.[20]   In the earlier part of the investigation, however, measurements of rotatory power were made with sodium light only, and, although interesting results (discussed in Chapter VII.) were obtained, it was considered highly desirable to widen the scope of the investigation by the use of light of other wave lengths.

III.

NATURAL ROTATORY DISPERSION.

Consideration must now be accorded to the subject of rotatory dispersion. This is a phenomenon which immediately forces itself on the notice of the investigator who uses multichromatic light in studying the behaviour of optically active substances between crossed Nicols. He finds it impossible, by rotation of the analyser, to extinguish completely a beam of polarised light after it has traversed a column of an optically active body. There is always an emergent beam which possesses a colour depending upon the position of the principal plane of the analyser, being, in fact, the complement of that which is extinguished for the particular setting of the analyser. He therefore resorts to spectroscopic analysis either of the incident or of the emergent light to enable him to concentrate his attention on light of one wave length at a time. One of the earliest of such methods to be devised was due to BROCH,[21] who used sunlight as his illuminant and resolved the beam emerging from the polarimeter by means of a prism. As this was in the days before the invention of the half shadow device, the appearance in the field of view of this arrangement was simply that of the solar spectrum crossed, of course, by the Fraunhofer dark lines. Rotation either of the polariser or of the analyser, however, caused a dark band—the extinction band—to enter the spectrum at one end and to move across it, finally leaving the field of vision at the other end. By adjusting the setting of the analyser so as to superpose the extinction band on the Fraunhofer lines in succession it is possible to make measurements of rotatory power throughout the visible spectrum. But this method is practically applicable only to the examination of substances which exhibit large rotations and even then is not very accurate. For the extinction band is not a sharply defined line, and it becomes broader and more diffuse as the rotation of the substance under examination becomes less, thus greatly imparing the accuracy of setting. Very material advances have, however, been made in the technique of polarimetry since these early times, and

it is now possible to obtain trustworthy and accurate measurements of the rotatory dispersion even of substances of very low rotatory power over a fairly wide spectral range. For this purpose the open and enclosed arcs mentioned in Chapter I., are used in conjunction with a direct-vision spectroscopic eyepiece, and, if necessary, a constant deviation prism to resolve the incident light.

BIOT'S discovery in 1815 of the rotatory power of organic compounds[22] was followed two years later by his announcement of a dispersion equation,[23] according to which " the rotation of the different simple rays is reciprocal to the square of their wave lengths." The French physicist used at least one light filter in his investigations, but even with this relatively crude apparatus, it was not long before he began to suspect that his law was not rigorously exact. Direct confirmation of his suspicions was obtained when, in 1886,[24] he endeavoured to compensate the laevo-rotation of a column of turpentine by means of a column of suitable length of dextro-rotatory oil of lemon. He found that he was able to obtain perfect compensation only for one wave length at a time, there being a small, but very distinct lack of compensation for all the others, thus proving that one, if not both, of these substances could not obey a one constant dispersion equation. Then, two years later,[25] he published a very long account of " Méthodes mathématiques et expérimentales, pour discerner les Mélanges et les Combinaisons, définies ou non définies, qui agissent sur la Lumière Polarisée ; suivies d'applications aux combinaisons de l'acide tartrique avec l'eau, l'alcool, et l'esprit de bois," in which he announced his discovery of the fact that tartaric acid, both in aqueous and in alcoholic solution, so far from following the inverse square law, actually increases in rotatory power with increasing wave length in some parts of the visible spectrum. He observed, further, that the rotatory power of such solutions was remarkably susceptible to small changes both of temperature and of concentration, and that under some conditions the rotatory dispersion curves of such solutions showed maxima. He even predicted the experimental conditions necessary for a change in the sign of the rotation of the acid, that is to say, the conditions under which its rotatory dispersion curve would be found to cross the axis of wave length, and, twelve years later,[26] verified his prediction in a very striking manner. He regarded these anomalies—the maxima and reversals of sign—in the rotatory dispersion curves of tartaric acid, however, merely as incidental manifestations of its abnormal behaviour,

and emphasised rather (as being a more important property of this remarkable compound) the extreme sensitiveness of its rotatory power to changes of solvent, concentration and temperature.

BIOT was then led to classify optically active substances under two heads :—

(a) the " quartz " type, in which the rotation increases with decreasing wave length, and generally follows the inverse square law fairly closely, and

(b) the " tartaric acid " type, in which the rotation increases with increasing wave length, at least in some part of the spectrum. Naturally, in this case the inverse square law is never followed, even approximately, in any accessible region of the spectrum.

Unfortunately, however, after his death, this logical line of investigation was generally abandoned, most of his successors putting forward and supporting views which were much less well-defined. A great deal of importance, for example, was attached to the appearance of a maximum or minimum in the rotatory dispersion curve of a compound, and to the manner in which this singular point on the curve behaved when the external experimental conditions were modified. A reversal of sign, too, was regarded as a point of almost equal importance to the maximum, though apparently no connection between these two singular points was ever suspected. The appearance of one of these two points then came to be regarded as a criterion for distinguishing between BIOT'S two types of active compound, although much confusion was caused by the varying interpretations placed on the different terms in use by the individual investigators.

The term " normal dispersion " was used to describe cases in which the rotation increases with decreasing wave length, and thus corresponds generally to the " quartz " type of BIOT. On the other hand, there appears to be no such agreement about the application of the term " anomalous dispersion." Originally introduced by LANDOLT[27] to describe the rotatory dispersion of tartaric acid, it obviously corresponds roughly to BIOT'S second or " tartaric acid " type. LANDOLT applied the term to the cases in which the rotatory power of nearly anhydrous tartaric acid and its concentrated solutions in alcohol changed in sign, and in which the maximum in the rotatory dispersion curves of aqueous solutions of this acid moved towards the less refrangible end of the spectrum with increasing concentration.

Other workers have applied this term in a less general way : for example, WINTHER[28] introduces a physiological distinction when he describes a dispersion curve as becoming " normal," in that the maximum passes into the ultra-violet." On the whole, it would appear best to regard the term " anomalous " as the strict opposite of " normal" and thus to restrict the application of the term to those cases only in which the rotatory power increases with increasing wave length. It then becomes necessary to specify the limits of wave length between which the dispersion is anamolous ; this done, the term acquires a precise and scientific meaning, from which, as will be shown later, a great deal of information may be deduced.

The inverse square dispersion law proposed by BIOT was, as we have seen, shown by him to be inexact. Although cases of anomalous rotatory dispersion could obviously not be represented by this law, several attempts were made, by increasing the number of arbitrary constants in the BIOT equation, to obtain an expression to fit the majority of the cases of substances exhibiting normal rotatory dispersion. The first of these was proposed by STEFAN,[29] in 1864,

$$\alpha = A + B/\lambda^2,$$

to fit the case of quartz. Several years later, in 1874, BOLTZMANN,[30] put forward another :—

$$\alpha = A/\lambda^2 + B/\lambda^4,$$

and, in 1881, LOMMEL[31] proposed a third :—

$$\alpha = k/\lambda^2 (1 - \lambda_0^2/\lambda^2)$$

These equations were all more in agreement with facts than the one proposed by BIOT, but they all broke down as experimental tests became more stringent.

In 1898, however, the German physicist DRUDE,[32] deduced a rotatory dispersion equation on theoretical grounds. The electronic theory treats light as a rapidly reversing electric force propagated through the ether. A material medium consists, of course, of molecules, every one of which is for the purpose of this theory considered to be capable of vibration either as a whole or in parts. A vibrating unit is generally called an " electron " which may or may not be identical with the electron generally understood to be an atom of negative electricity. A definite knowledge of the nature of these electrons is, however, unnecessary for the development of our subject. They may be considered merely as electrically charged particles which may or may not be material—they may be electric charges only—and they must be regarded as having fixed positions of equilibrium with

regard to the molecules to which they belong. That is to say that these electrons can in no wise conduct an electric current, but rather that the application of a steady electric force will displace them till the force of restitution called into play by the displacement just neutralises the displacing force ; when this has occurred, the motion ceases, and there is no further movement until the force is removed. When this occurs, the electrons will resume their former positions of equilibrium after having vibrated about them till the energy communicated to them by the disturbing force has been dissipated. An alternating electric force will, therefore, excite vibrations in the electrons of the medium. DRUDE considered that the effect of the asymmetry of form of a medium in producing optical activity was due to the fact that this asymmetry caused the electrons under the influence of light to execute vibrations in a spiral path. By making various simplifying assumptions, DRUDE deduced mathematically the rotatory dispersion equation which bears his name :—

$$a = \Sigma\, k_0 / (\lambda^2 - \lambda_0^2)$$

Each term of this equation thus contains two constants, k_0, which may be regarded as the rotation parameter, and λ_0^2, which may be regarded as the dispersion parameter. λ_0, however, has a wider significance than this ; it is the wave length of the disturbance corresponding to the frequency at which the electron is capable of absorbing energy. For any particular medium, therefore, there will be one term in the DRUDE equation corresponding to every electron causing rotatory dispersion, and every such term will contain in the denominator a constant which is the square of the wave length of the disturbance corresponding to the free period of this electron. It would appear impossible, however, for the vibrating unit to possess a mass anything like so great as that of a molecule or even of an atom, at least where absorption bands in the ultra-violet region of the spectrum are concerned. This becomes evident at once when it is considered that a frequency of 10^{15} periods per second is required for the production of an absorption band at $\lambda = 3,000$ A.U. in the near ultraviolet.

This equation was not immediately applied to practical use. When it was proposed, there were few experimental data of sufficient accuracy to test its validity and it was not till 1912, or thereabout, that it was applied to organic compounds. It is interesting to note that the earlier dispersion equations can all be derived as special cases of the DRUDE equation, a fact which no doubt accounts for their partial, if shortlived, success. Now, however, accurate data for the study of rotatory

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This equation was not immediately applied to practical use. When it was proposed, there were few experimental data of sufficient accuracy to test its validity and it was not till 1912, or thereabout, that it was applied to organic compounds. It is interesting to note that the earlier dispersion equations can all be derived as special cases of the DRUDE equation, a fact which no doubt accounts for their partial, if short-lived, success. Now, however, accurate data for the study of rotatory

dispersion have been accumulated for many years ; mainly under the direction of LOWRY, first at Guy's Hospital, London, and later at the University, Cambridge ; of PICKARD and KENYON, first at the Technical School, Blackburn, and later at Battersea Polytechnic, London ; and of PATTERSON, at the University, Glasgow, and, more recently, by AUSTIN, of the Westminster Training College, London, and WOOD and his co-workers at the University, Birmingham. Work of this nature is also being carried out abroad under RUPE at Basle, and, until his death, was being carried on under TSCHUGAEV in Russia. Work having a direct bearing on the problems of rotatory dispersion now under consideration was, however, carried on mainly by the three first-mentioned schools, and as the class of work attempted and the methods of obtaining results differ widely, it is advisable to bear the following facts in mind when such results are considered.

The method of LOWRY.—Measurements are made at one temperature only, and few solvents are employed. Light of very many different refrangibilities is employed, and observations are carried out in the ultraviolet by photographic methods. Efforts are directed mainly to the determination of the dispersion equation with the greatest possible accuracy, and refined experimental methods are used in order to attain this end.

The method of PICKARD *and* KENYON.—The method adopted by these investigators is to examine all compounds in the liquid state for light of as many different wave lengths as possible up to seven or eight and quite recently the photographic method of exploring the ultraviolet has been adopted. Observations of rotatory power are carried out at temperature intervals of 15-20° C. from 15° to about 160 or 180° C. and more reliance is placed on results from the smoothed experimental curves than on any single measurement. Solvents are employed if possible, but in rather a desultory way, and measurements in solution never replace those in the homogeneous state. It will be seen that this method, whilst not nearly so accurate nor so searching as LOWRY'S, yet possesses the advantage over his that it takes into account the influence of temperature, and, further, it is less laborious and allows of the examination of a larger number of compounds. It does not claim to investigate the effect of solvents on rotatory power, and in this respect has little in common with the work of PATTERSON.

The method of PATTERSON.—This investigator has worked mainly with derivatives of tartaric acid, and confines his attention to the study of the rotatory power of a few compounds in many solvents He works with light of three or four refrangibilities and employs temperatures up to 200° C. when possible. He has possibly the most difficult task of all three schools because he has to disentangle so many different effects. His results and conclusions demand the most attentive and detailed examination, if only because of the fact that he refuses to admit the validity of the DRUDE equation and treats the subject of rotatory dispersion from an entirely different viewpoint.

It has been found that the rotatory dispersion of the vast majority of optically active organic compounds can be represented by an equation of the DRUDE type containing only one term, and that such an equation with two terms is adequate to express the rotatory dispersion of the few remaining cases. LOWRY[33] has, therefore, proposed the classification of optically active compounds into two types.

(*a*) Compounds whose rotatory dispersion can be expressed by a one term DRUDE equation are said to exhibit " simple " rotatory dispersion.

(*b*) Compounds which require a DRUDE equation with more than one term in order to express their rotatory dispersion are said to exhibit " complex " rotatory dispersion. As a fact, it is found that organic compounds all possess such relatively low rotatory powers that the present methods of polarimetry are not sufficiently delicate to detect more than two terms in such an equation, so that, in practice, the distinction between simple and complex rotatory dispersion amounts to a distinction between a one term and a two term DRUDE equation.

With these definitions before us, it is now possible, either by graphical or formal mathematical analysis, to examine the connection between simple, complex, normal and anomalous rotatory dispersion. The graphical method may be considered first.

Simple Rotatory Dispersion.—If a is plotted against λ, this case gives two branches of a hyperbola-like curve, asymptotic to the lines $\lambda = \lambda_0$ and $a = 0$, one branch lying wholly in the positive region of the graph, and the other wholly in the negative. As it has been found that absorption bands in the infra-red exercise little or no influence on the rotatory dispersion, only cases with bands in the ultra-violet

will be considered. Fig. 1 shows a typical curve for simple rotatory dispersion. The value of α passes instantaneously from $+$ infinity to $-$ infinity as λ in decreasing passes through the value λ_0. On both sides of λ_0, the rotatory dispersion is normal, and on the side of greater wave length follows the inverse square law more and more closely as λ_0 is decreased.

FIG. 1.   FIG. 2.

VISIBLE REGION

$\alpha = 1/(\lambda^2 - 0.09)$

VISIBLE REGION

$\alpha = 1/(\lambda^2 - 0.09) + 1/(\lambda^2 - 0.04)$

VISIBLE REGION

$\alpha = 2/(\lambda^2 - 0.09) - 1/(\lambda^2 - 0.04)$

VISIBLE REGION
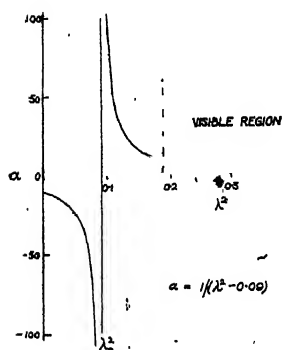
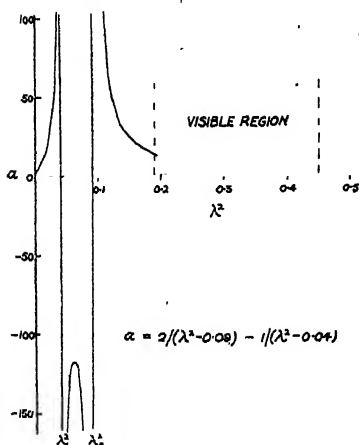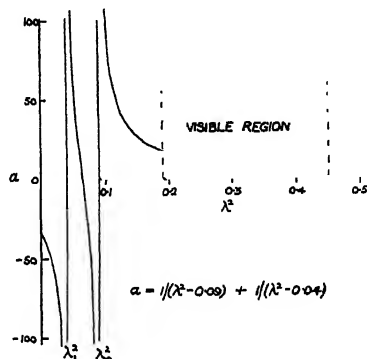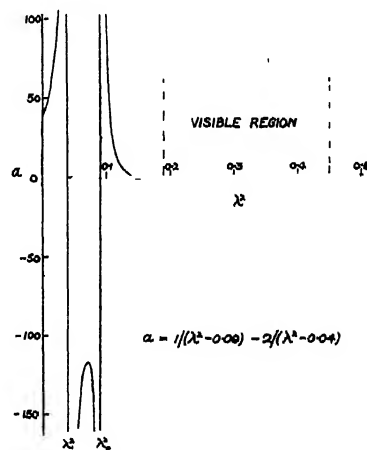$\alpha = 1/(\lambda^2 - 0.09) - 2/(\lambda^2 - 0.04)$

FIG. 3.   FIG. 4.

Complex Rotatory Dispersion.—There are two cases of complex rotatory dispersion to consider.

(a) *The two terms have the same sign.*

In this case the resultant curve is the sum of the two component hyperbola-like curves. Inspection of Fig. 2 shows that the dispersion is always normal on the greater wave length side of the band nearest the region of experimental observation, and that α assumes the value $\pm$ infinity on crossing each band.

(b) *The two terms have opposite signs.*

In this case the resultant curve is the difference of the two components, and the method of classification here adopted now necessitates a further subdivision.

(1) k_0 *is greater than* k_1, *and* λ_0 *greater than* λ_1.

An inspection of Fig. 3 indicates that the term containing k_0 and λ_0 always dominates the other term in the resultant dispersion curve, so that the dispersion is always normal on the greater wave length side of the more accessible band.

(2) k_0 *is less than* k_1, *and* λ_0 *greater than* λ_1.

In this case, shown in Fig. 4, it is evident that the k_1 term dominates the k_0 term for values of λ remote from λ_0, but that as the value of λ decreases, the resultant dispersion curve shows first of all a point of inflexion as the influence of the k_0 term begins to make itself more distinctly felt. As λ decreases still further, the k_0 term becomes the dominant one, causing a maximum in the resultant curve, and, finally, as λ decreases still further, the numerical values of the terms become equal in amount and opposite in sign, causing α to assume a zero value, after which the k_0 term dominates the other so completely that it imposes its own sign on the resultant dispersion curve. The region between the maximum and the reversal of sign is obviously one of anomalous dispersion—at all other points on the curve on the greater wave length side of the more accessible band it is normal.[*] It will, moreover, be

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[*] This raises a rather debatable point. The classification of the dispersion in this case depends on whether the compound is considered to be laevo- or dextro-rotatory. If it be assumed laevo-rotatory, then the whole region between the maximum and the asymptote must be regarded as one of anomalous dispersion since the laevo-rotation is decreasing with wave length. Considered numerically, however, without regard to the sign of the rotation, then the above statement is correct. (*Vide* p. 27.)

observed that in this, as in all the other cases, a assumes an infinite value at the head of each absorption band, and changes sign in crossing it.

Other Types of Anomalous Dispersion.—In no case up to the present has the portion of the curve on the short wave length side of the more accessible absorption band been considered. The reason for this is that no compound has yet been examined in which this region is accessible to exact experimental investigation, so that it is at present only of theoretical interest. It is clear, however, from an examination
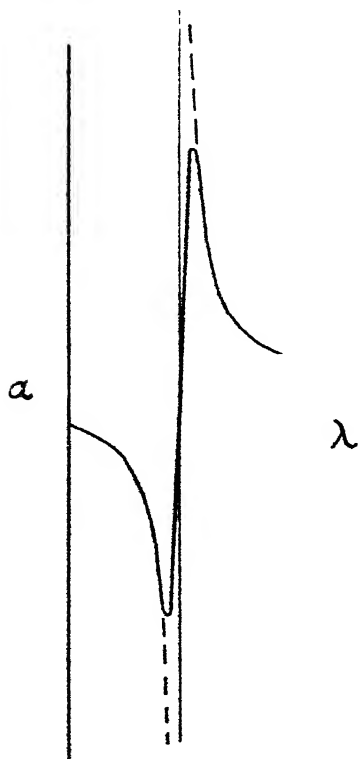

Fig. 5.

of Figs. 1-4, that further types of anomalous dispersion should be discovered when the rotatory power of compounds can be examined in regions of the spectrum on the short wave length side of a rotatory absorption band.

(a) *Anomalous dispersion on crossing a band.*

Insofar as the rotatory power of a substance changes from $+$ infinity to — infinity when λ decreases through the value λ_0, it may be argued that as the value of α decreases with decreasing wave length, the substance is here exhibiting anomalous dispersion over an infinitely small range of wave length. But it is nearly certain that the range of wave length over which such anomalous dispersion is exhibited, though small, is finite. For the DRUDE equation is actually the equation of a forced vibration in which the damping effect due to absorption—the degradation of the light energy into heat—is neglected. But in the near neighbourhood of the absorption band, this friction term cannot be ignored, and the DRUDE equation in its simplified form will break down completely. The actual dispersion curve will probably have some such form as that shown in Fig. 5. It may confidently be expected, however, that the DRUDE equation in its present simplified form will express the facts very closely indeed up to within two or three Ångström Units of the head of a band, and, as it has not yet been possible to make polarimetric measurements within about 400 A.U. of the head of a band, it is very unlikely that the effect of this friction term will be detected, at all events with our present methods.

(b) *Spurious anomalous dispersion on the more refrangible side of an absorption band.*

Examination of the curves in Figs. 1-4 makes evident at once the futility of applying the terms dextro- and laevo-rotatory to a non-transparent optically active compound, provided that the regions on both sides of the absorption band are accessible to polarimetric measurement. Fig. 1 illustrates the simplest case in point. On the greater wave length side of the band it is dextro-rotatory ; on the lesser wave length side it is laevo-rotatory. Furthermore, unless it be agreed to consider the substance dextro-rotatory for all wave lengths (that is, to regard a laevo-rotation as a negative dextro-rotation) because it is dextro-rotatory on the greater wave length side of the band, it follows that on the other side, its dispersion must be anomalous in that its laevo-rotatory power decreases with decreasing wave length. It is suggested that the term " spurious " be applied to anomalous dispersion of this type. Spurious anomalous dispersion can also be found in Figs. 2-4.

(c) *True anomalous dispersion in the region between two absorption bands.*

If the region between the absorption bands in Fig. 4 be examined, it immediately becomes evident that whatever sign we ascribe to the rotatory power of the compound, one of the arms of the loop in the dispersion curve must be regarded as exhibiting anomalous dispersion.

These other types of anomalous dispersion, whilst interesting from a theoretical point of view, are hardly likely ever to be realised experimentally, and so require no further consideration here.

There remains now to be presented a formal deduction of the connection between simple, complex, normal and anomalous rotatory dispersion. It is, of course, obvious at once that a simple dispersion curve can never be anything else but normal. Of the types of complex equation, it is again evident that the one in which the terms possess the same sign can never exhibit other than normal dispersion. What, then, are the criteria for anomalous rotatory dispersion with a two term DRUDE equation in which the terms differ in sign ? It is known that a reversal of sign, a maximum and a point of inflexion are three singular points on the dispersion curve which, either separately or together, often accompany anomalous dispersion.[34]

Consider the equation[35] :—

$$\alpha = k_0/(\lambda^2 - \lambda_0^2) - k_1/(\lambda^2 - \lambda_1^2)$$

for a change of sign, $\alpha = 0$

and $$\frac{k_0}{\lambda^2 - \lambda_0^2} = \frac{k_1}{\lambda^2 - \lambda_1^2}$$

i.e. $$\frac{k_0}{k_1} = \frac{\lambda^2 - \lambda_0^2}{\lambda^2 - \lambda_1^2}$$

With λ_0 and λ_1 in the ultra-violet, *i.e.*, both less than λ, this condition will be satisfied for a finite value of λ only when

(a) $\lambda_0 > \lambda_1$ if $k_1 > k_0$

or, conversely,

(b) $\lambda_0 < \lambda_1$ if $k_1 < k_0$

for a maximum, $$\frac{d\alpha}{d\lambda} = 0,$$

$$\frac{d\alpha}{d\lambda} = -\frac{2k_0\lambda}{(\lambda^2 - \lambda_0^2)^2} + \frac{2k_1\lambda}{(\lambda^2 - \lambda_1^2)^2}$$

therefore $$\frac{2k_0\lambda}{(\lambda^2 - \lambda_0^2)^2} = \frac{2k_1\lambda}{(\lambda^2 - \lambda_1^2)^2}$$

i.e.
$$\frac{k_0}{k_1} = \left\{ \frac{(\lambda^2 - \lambda_0^2)}{(\lambda^2 - \lambda_1^2)} \right\}^2$$

This can be satisfied by the same conditions as for a reversal of sign.

for a point of inflexion,
$$\frac{d^2 a}{d\lambda^2} = 0,$$

but
$$\frac{da}{d\lambda} = -\frac{2k_0\lambda}{(\lambda^2 - \lambda_0^2)^2} + \frac{2k_1\lambda}{(\lambda^2 - \lambda_1^2)^2}$$

put
$$(\lambda^2 - \lambda_0^2) \text{ etc.} = x_0, \text{ etc.}$$

then
$$\frac{da}{d\lambda} = -\frac{2k_0\lambda}{x_0^2} + \frac{2k_1\lambda}{x_1^2}$$

and
$$\frac{d^2 a}{d\lambda^2} = -2\left[\frac{-k_0}{x_0^2} + \frac{k_1}{x_1^2}\right] - 4\lambda^2\left[\frac{-2k_0}{x_0^3} + \frac{2k_1}{x_1^3}\right]$$

therefore
$$\frac{d^2 a}{d\lambda^2} = \frac{-2k_0}{(\lambda^2 - \lambda_0^2)^2} + \frac{2k_1}{(\lambda^2 - \lambda_1^2)^2} + \left[\frac{4k_0\lambda}{(\lambda^2 - \lambda_0^2)^3} - \frac{4k_1\lambda}{(\lambda^2 - \lambda_1^2)^3}\right]2\lambda$$

$$= -\frac{2k_0(\lambda^2 - \lambda_0^2) - 8k_0\lambda^2}{(\lambda^2 - \lambda_0^2)^3} + \frac{2k_1(\lambda^2 - \lambda_1^2) - 8k_1\lambda^2}{(\lambda^2 - \lambda_1^2)^3}$$

$$= \frac{2k_0(3\lambda^2 + \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^3} - \frac{2k_1(3\lambda^2 + \lambda_1^2)}{(\lambda^2 - \lambda_1^2)^3}$$

$$= 0$$

$$\therefore \frac{2k_0(3\lambda^2 + \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^3} = \frac{2k_1(3\lambda^2 + \lambda_1^2)}{(\lambda^2 - \lambda_1^2)^3}$$

or
$$\frac{k_0}{k_1}\frac{(3\lambda^2 + \lambda_0^2)}{(3\lambda^2 + \lambda_1^2)} = \left\{\frac{\lambda^2 - \lambda_0^2}{\lambda^2 - \lambda_1^2}\right\}^3.$$

which can be satisfied by the same conditions as those for a reversal of sign or a maximum. It thus becomes apparent that these three singular points on the dispersion curve must all appear and disappear together, and that the appearance of one is a certain indication of the presence of the other two, although they may not be experimentally realised.

IV.

COMPLEX ROTATORY DISPERSION — THE CHARACTERISTIC DIAGRAM.

In Chapter III., it was shown that anomalous rotatory dispersion can occur if, and only if, three conditions are fulfilled :—

(*a*) the dispersion equation contains two terms,

(*b*) the two terms have opposite signs, and

(*c*) k_0 is greater than k_1 when λ_0 is less than λ_1, or conversely.

It is also obvious that the term " anomalous " as applied to rotatory dispersion is one that requires very careful definition, but that if its meaning and limitations be clearly understood, it is possible to use it to convey a good deal of qualitative information about the nature of the dispersion curve. For, if a compound is known to exhibit anomalous rotatory dispersion, it can be asserted that the three conditions given above are fulfilled, and that, in addition, the dispersion curve will show :—

(1) a reversal of sign,

(2) a maximum, and

(3) a point of inflexion.

When quantitative information is required, however, it is necessary to employ LOWRY'S method of classification of rotatory dispersion into simple and complex. This investigator has proposed[36] the terms " rotation constant " and " dispersion constant " for k_0 and λ_0^2, respectively, in the DRUDE equation. This proposal offers distinct advantages when dealing with substances exhibiting simple rotatory dispersion, for, by making $\lambda = \sqrt{1 + \lambda_0^2}$, and calling this the "absolute" wave length, k_0 becomes numerically, though not dimensionally equal to a, and it then becomes possible to compare the rotatory powers of substances at what are probably corresponding conditions of wave length : that is to say, the effect of dispersion can be eliminated entirely. The suggestion may be summarised thus :—

For simple rotatory dispersion,

k_0 is the rotation constant,
λ_0^2 is the dispersion constant,
$\sqrt{1 + \lambda_0^2}$ is the absolute wave length,
and $\alpha_{abs.}$ is numerically equal to k_0.

It is then surely reasonable to hope that k_0 will prove a much more accurate measure than α of the true asymmetry of the molecule. Furthermore, provided that we are certain that we are dealing with a case of simple rotatory dispersion, the rotation and dispersion constants can be calculated from determinations of rotatory power with light of two wave lengths only, so that it is not a difficult matter to determine k_0 for such a case.

With complex rotatory dispersion, however, the case is very different. Four arbitrary constants are required for a two term equation, and, even when they can be determined, it is at present impossible to treat them in such a way as to eliminate the effect of dispersion on the rotatory power. What, then, is the chemical significance of complex rotatory dispersion ? All that the DRUDE equation tells us is that two absorption bands are concerned in producing the dispersion. These bands must be produced either by one electron with two different free periods, or by two electrons, each with its own free period. It is impossible to decide *a priori* which is the case, but by adopting the latter alternative, a certain amount of progress can be made. The question then arises—are these electrons situated in one molecule or in two ? This question immediately recalls BIOT'S classical experiment with turpentine and oil of lemon (p. 18). These substances exhibit rotatory dispersion which is nearly simple and have rotatory powers which are opposite in sign. By passing a beam of polarised light through successive tubes of these liquids, BIOT succeeded in producing anomalous, and hence complex, rotatory dispersion. In another experiment,[37] he dissolved dextrorotatory camphor in laevo-rotatory turpentine with a similar result. It is, of course, illogical to argue that because a phenomenon can be imitated in a certain way, it always occurs in that way, but these experiments undoubtedly furnish good ground for a working hypothesis. It will be assumed, then, that for a substance to exhibit complex rotatory dispersion there must be present two kinds of molecule, each of which exhibits simple rotatory dispersion. It is necessary, of course, that these molecules shall possess different dispersive powers, otherwise the sum of their

simple rotatory dispersive powers will merely produce a simple rotatory dispersion curve with the same asymptotes.

There are several conceivable ways in which these two kinds of molecule can be produced :—

(a) Deliberate mixture of different substances,
(b) Simple and associated molecules of the same compound,
(c) Simple and dissociated molecules of the same compound,
(d) Formation of solvates in solution,
(e) Isomerism.

Examples can be found to fit any one of these alternatives, but by dealing only with pure liquids, it is possible to eliminate (a) and (d) entirely, and (e) nearly completely. With the majority of the compounds dealt with in this thesis, (b) and (c) are unlikely factors, so that we are compelled to attribute complex rotatory dispersion to a dynamic form of isomerism which is too labile in general to be detected by ordinary chemical methods.

The idea of explaining anomalous dispersion by the unequal counterbalancing action of two components of opposite rotatory power and unequal dispersive power was first put forward in 1858 by ARNDTSEN,[38] as follows :—

" Or si l'on imagine deux corps actifs qui n'agissent pas chimiquement l'un sur l'autre, dont l'un tourne le plan de polarisation à droite, l'autre à gauche, et en outre que la rotation du premier augmente (avec la réfrangibilité de la lumière) plus vite que celle de l'autre, il est clair qu'on aura, en mèlant ces corps en certaines proportions, des combinaisons qui montreraient des phénomènes optiques tout à fait semblables à ceux de l'acide tartrique, ce que M. BIOT a déja prouvé par ses recherches sur différents mélanges d'essence de térèbenthine et de camphre naturel. On pourrait donc regarder l'acide tartrique comme un mélange de deux corps différent seulement à l'égard de leurs propriétés optiques, dont l'un aurait un pouvoir rotatoire négatif, l'autre un pouvoir rotatoire positif, et dont les rotations varieraient avec la réfrangibilité de la lumière en proportions différentes."

Practically the same thing expressed in a slightly different way in order to give prominence to the idea of solvate formation, was put forward in 1881 by H. E. ARMSTRONG,[39] when he wrote that :—

" The most probable explanation of the anomalous rotatory dispersive power of solutions of tartaric acid would appear to be that they contain, besides the acid, a compound of opposite rotatory power

of the acid with water in proportions varying according to the concentration and temperature of the solutions."

This hypothesis, now nearly seventy years old, was treated graphically in 1913 by ARMSTRONG and WALKER,[40] who propose what they call a " characteristic diagram." Four cases are considered of the rotatory properties of a liquid substance containing two bodies of different optical behaviour :—

- (i.) Two substances having rotatory powers of the same sign and the same dispersive power.
- (ii.) Two substances having rotatory powers of the same sign but different dispersive powers.
- (iii.) Two substances having rotatory powers of opposite sign but the same dispersive power.
- (iv.) Two substances having rotatory powers of opposite sign and also different dispersive powers.

These cases can now be treated graphically by making the assumption that the rotatory power of each constituent form is constant under all conditions. The authors promise to discuss the legitimacy of this assumption later on, but apparently they have not yet done so. Its legitimacy is in most cases very doubtful indeed, but the method is inherently sound because another assumption, which is supported by fact, can be made which preserves intact all the good points of the method. (*See* p. 42).

In the diagrams, rotatory power is represented by the ordinates and percentage composition by the abscissae. R_1, G_1 and B_1, represent the rotatory powers of one form or constituent for red, green and blue light respectively : R_2, G_2 and B_2 have the same significance for the other constituent form.

Case I.

Because the constituents have the same dispersive power, that is, because $\dfrac{G_1}{R_1} = \dfrac{G_2}{R_2}$ or $\dfrac{B_1}{R_1} = \dfrac{B_2}{R_2}$, etc., and because by hypothesis the rotations of the constituents are unaffected by external conditions, the rotation-composition curves of the mixture for light of different colours will be straight lines intersecting on the line of zero rotation, but outside the diagram (Fig. 6). This point of intersection will thus have no physical significance. The dispersion of the mixture will always be normal.

Case II.

The rotation-composition curves will be straight lines as before, but as the dispersive powers of the components are not the same, $\frac{G_1}{R_1} \neq \frac{G_2}{R_2}$, etc., and they will not intersect on the line of zero rotation,
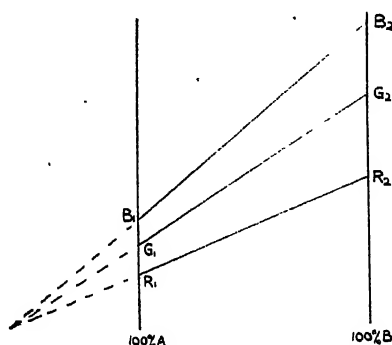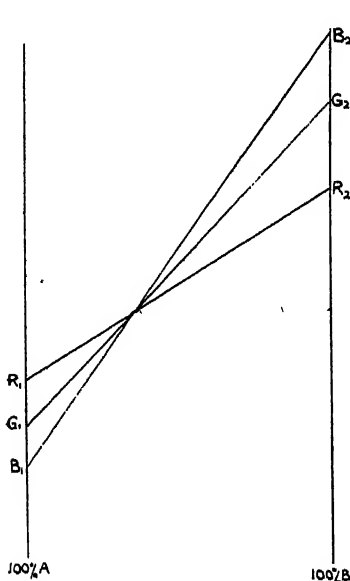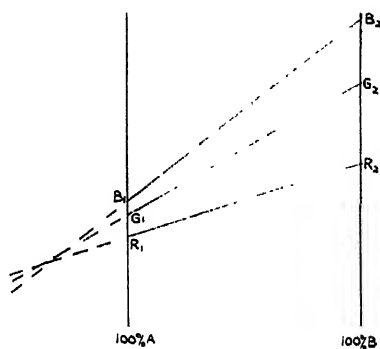
FIG. 6.   FIG. 7.
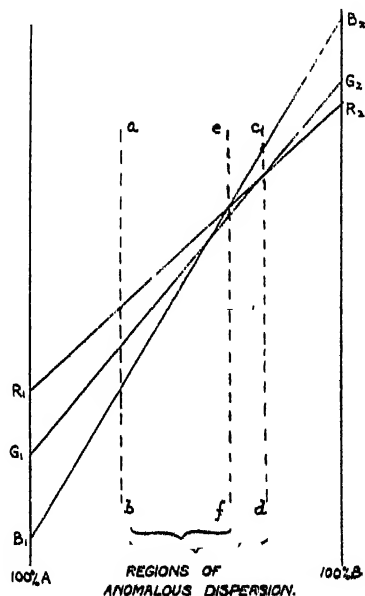
FIG. 8.   FIG. 9.

nor will they necessarily intersect all at one point. The points of intersection have, as in Case I., no physical significance, and the dispersion of the mixture will be normal. (Fig. 7).

Case III.

By the same arguments as for Case I., the linear rotation-composition curves will intersect at a point on the line of zero rotation, but this time at a point within the diagram. At the particular composition represented by this point, therefore, the mixture will be optically inactive for all colours of light. On one side of this point, too, it will be dextro-rotatory for all colours of light, whilst on the other side, it will be similarly laevo-rotatory. Its dispersion will, however, always be normal. (Fig. 8.)

Case IV.

This is similar to Case II., except that the lines here intersect at points within the diagram. In this case the lines do not intersect on the line of zero rotation, nor need they all intersect at one point. Examination of Fig. 9 shows that in the region between the lines *a b* and *c d*, the rotation for green light is less than that for red, so that the dispersion is anomalous for those two colours. For blue and red the region is bounded by the lines *a b* and *e f*. Here we are confronted with the same difficulty as that dealt with in the footnote to p. 25 —consider, for example, that portion of the diagram immediately to the right of *a b*. The red rotation is small and positive, the blue rotation is large and negative, so we say that the dispersion is anomalous, that is, that the blue rotation is less (algebraically) than the red. In the portion of the diagram immediately to the left of *a b*, the red rotation is small and negative, whilst the blue rotation is large and negative. The blue rotation is thus still algebraically less than the red, but because both the rotations happen to possess the same sign, their magnitudes are considered numerically and the dispersion is said to be normal.

Application of the Characteristic Diagram.

The characteristic diagram has been applied to experimental results almost entirely by PICKARD and KENYON.[41] Their application of it has been admittedly empirical, and it is to be feared that some of the results they have achieved with it have been due very largely

to fortuitous coincidence because they are not borne out by deductions drawn from the application of the DRUDE equation to the same experimental figures.

Two assumptions must be made before the characteristic diagram for any particular optically active liquid can be constructed :—

(a) That the apparently homogeneous liquid contains two optically active constituents, and

(b) That the rotatory power of each separate constituent is unaltered by changes of external conditions such as solvent, concentration and temperature.

It is obvious then, that the characteristic diagram can be obtained by plotting rotatory powers as ordinates and rotatory powers under the same experimental conditions with some arbitrarily chosen wave length as abscissae. In effect, this procedure amounts to the same thing as plotting rotatory powers for light of different refrangibilities in one vertical line for a given set of experimental conditions. The diagram arrived at by this method will then show rotatory power as ordinate and percentage composition of the mixture of dynamic isomerides to an unknown scale as abscissa. This may best be illustrated, perhaps, by a concrete example.

Suppose that the rotatory power of an optically active liquid has been measured for light of three different colours—yellow, green and violet—under different experimental conditions, for example at 20° and 150° C. in the homogeneous state, and at 20° C. in 5 per cent. solution in alcohol, carbon bisulphide and in pyridine. The following table gives the hypothetical results :—

	$[a]_{yell.}$	$[a]_{gr.}$	$[a]_{vi.}$
Homogeneous at 20°	22°	30°	48°
Homogeneous at 150°	15°	20°	29°
5% solution in alcohol	20°	27°	43°
5% solution in pyridine	+ 8°	+ 2°	— 4°
5% solution in carbon bisulphide .	— 2°	— 5°	—17°

The green line is chosen as the arbitrary standard, and rotations are plotted on Fig. 10 along ordinates and abscissae. The green line on the characteristic diagram will, therefore, of necessity, be straight with a slope of unity. Now the figures for the rotatory power in the homogeneous state at 20° C. are taken. $[a]_{yell.} = 22°$: with this as ordinate and the corresponding value $[a]_{gr.} = 30°$ as abscissa, the point a is plotted. Again, $[a]_{vi.} = 48°$: with this as ordinate,.

and $[\alpha]_{\text{gr.}} = 30°$ as abscissa, the point b is plotted, and so on. A series of points is thus obtained for yellow rotations, and another for the violet, which are seen to fall on straight lines. This is the required characteristic diagram, and the fact that straight lines are obtained in
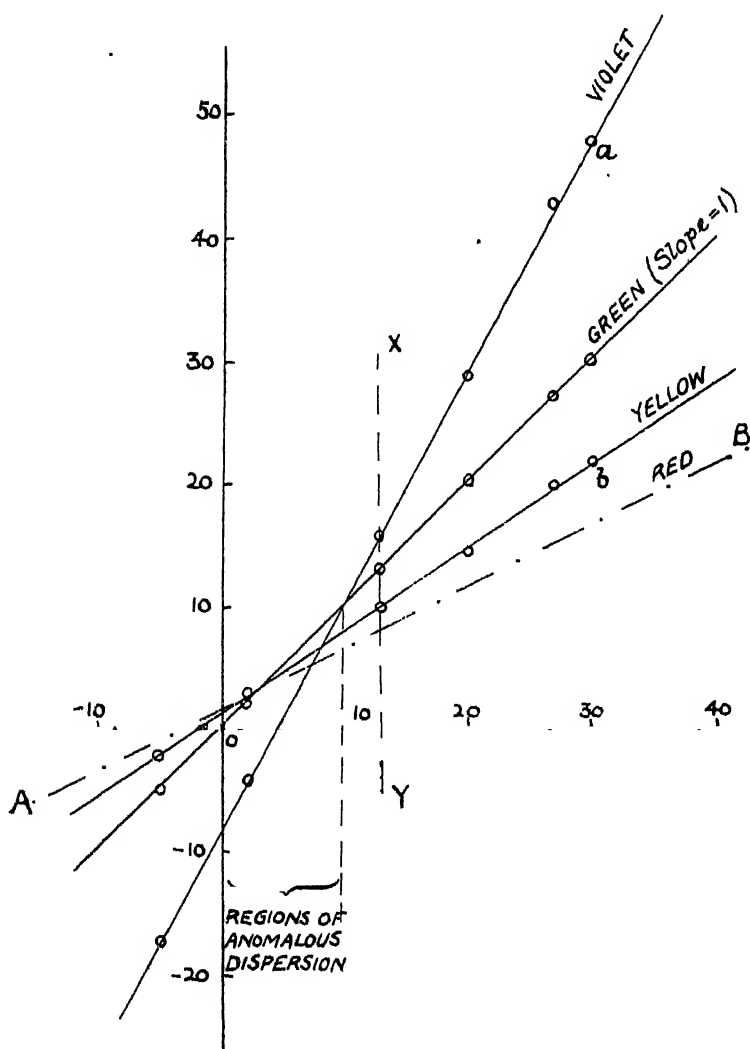
FIG. 10.

most cases is some indication that for those cases the initial assumptions are justified. From this diagram, several deductions may be made :—

(1) Suppose that in some solvent at a certain concentration and temperature it is found that $[\alpha]_{vi.} = 16°$. It seems legitimate to infer that under these conditions its rotations for other wave lengths will lie on the line X Y, and that $[\alpha]_{gr.}$ will be 13° and $[\alpha]_{yell.}$ will be 10·5.°

(2) Rotations measured for a line in the red region of the spectrum will no doubt lie on some such line as A B.

(3) If, for any given set of experimental conditions, $[\alpha]_{gr.}$ is less than + 8·5° and greater than zero, the dispersion under those conditions will be anomalous, and, further, anomalous dispersion can not occur unless this condition is fulfilled. It is important to note how the extent of the region of anomalous dispersion depends on the wave lengths of the light considered. For example, when the portion of the spectrum extending from yellow to violet is considered, the region of anomalous dispersion extends from $[\alpha]_{gr} = + 8·5°$ to $[\alpha]_{gr.} = 0$: if, however, measurements are confined to the region of the spectrum extending only from the yellow to the green, the region of anomalous dispersion would extend only from $[\alpha]_{gr.} = + 5·5°$ to $[\alpha]_{gr.} = 0°$.

(4) The characteristic diagram can be used to determine the configuration of an active body. PICKARD and KENYON have made a great point of the fact that compounds of similar constitution have the same characteristic diagram.[42] The truth of this will be discussed later, but for the moment, it will be assumed. Suppose that one characteristic diagram can be constructed for all derivatives of a compound with a dextro configuration. Then the characteristic diagram for derivatives of its optical isomeride will be the mirror image of this. The two diagrams are represented in Figs. 11 and 12. Now suppose that a derivative A of the d-compound is made and it is found to have rotations of $[\alpha]_{yell.} = - 1°$: $[\alpha]_{gr.} = - 7°$, and $[\alpha]_{vi.} = - 31°$. The question arises—has an inversion taken place during the reaction giving rise to the compound A, that

Fig. 11.

CHARACTERISTIC DIAGRAM
FOR
d-ISOMERIDE

CHARACTERISTIC DIAGRAM
FOR
l-ISOMERIDE
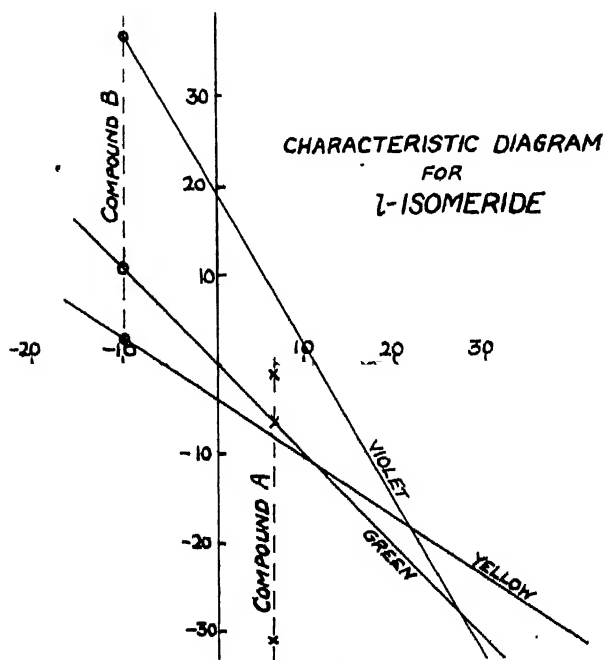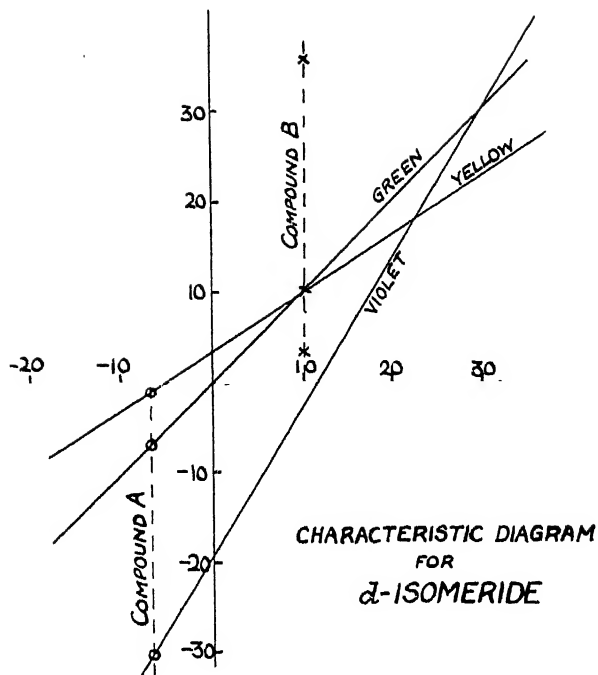
Fig. 12.

is, is A really a derivative of the *l*-parent compound, or has the rotation merely been depressed so that A is a laevo-rotatory derivative of the *d*-compound ? In order to decide the point, the rotations are plotted on both diagrams and it is found that they fit on the *d*-diagram but not on the *l*-. Therefore, no inversion has taken place and A is a laevo-rotatory compound with the *d*-structure. With the compound B, however, with $[\alpha]_{\text{yell.}} = +3°$: $[\alpha]_{\text{gr.}} = +10°$, and $[\alpha]_{\text{vi.}} = +36°$, it is found that, although it is a dextro-rotatory derivative of a *d*-compound, its rotations fit only on the *l*-diagram, and so it must be regarded as possessing the *l*-structure.

In actual practice, however, matters are not as simple as this, for the lines on the diagram generally intersect so close to the line of zero rotation that a diagram is nearly identical with its mirror image and it becomes a matter of difficulty to decide which diagram is best fitted to accommodate the experimental figures in question.

The above method of plotting the characteristic diagram has been modified by PATTERSON,[43] with the result that greater accuracy can be obtained in a smaller space. PATTERSON plots, not rotations for all wave lengths against rotations for some standard wave length, but differences between the standard rotations and the others against the rotations for the standard wave length. The standard reference line is then drawn horizontally, and positive differences are measured above it, negative ones below. By adopting this method, one can exaggerate the vertical scale with reference to the horizontal, and thus construct an accurate diagram without a corresponding increase in size.

An example will make the method clear. Consider the figures on p. 36. The green line is taken as standard again, and the figures are first of all recalculated thus :—

	$[\alpha]_{\text{yell.}} - [\alpha]_{\text{gr.}}$	$[\alpha]_{\text{gr.}}$	$[\alpha]_{\text{vi.}} - [\alpha]_{\text{gr.}}$
Homogeneous at 20°	— 8°	+30°	+18°
Homogeneous at 150°	— 5°	+20°	+ 9°
5% solution in alcohol	— 7°	+27°	+16°
5% solution in pyridine	+ 1°	+ 2°	— 6°
5% solution in carbon bisulphide .	+ 3°	— 5°	—12°

These values are plotted on Fig. 13 to give a characteristic diagram which is in all respects comparable with that on p. 37 (Fig. 10). It will readily be seen that, although the diagram occupies no more room than Fig. 10, yet it is on a very much larger scale, and, particularly,
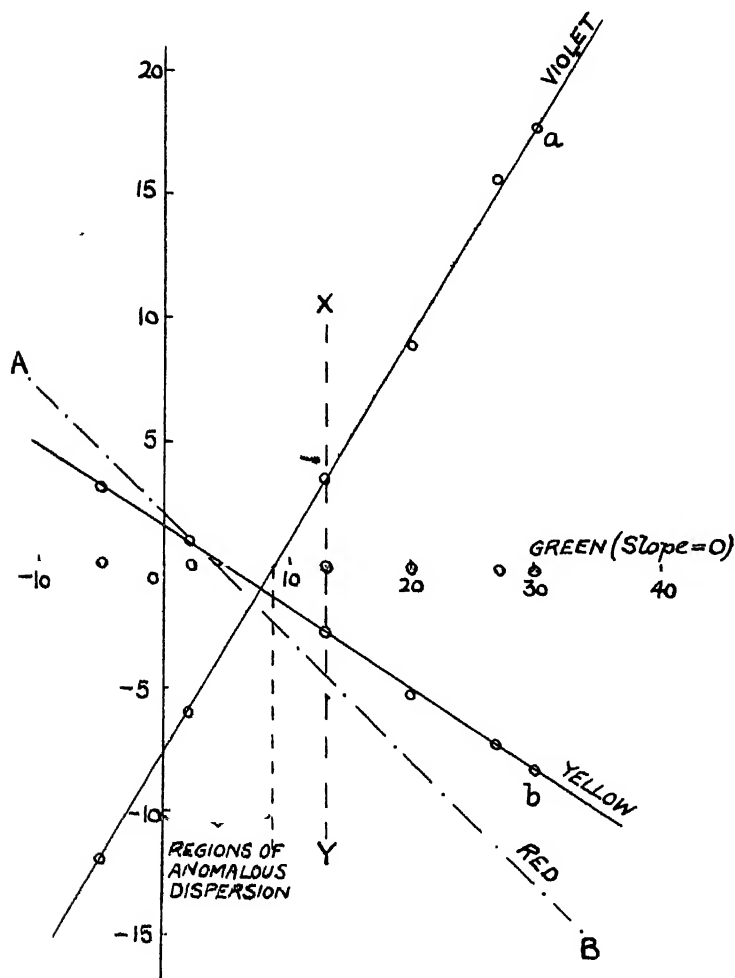
FIG. 13.

the lines intersect at angles which are very much less acute, thus enabling, for example, the limits of the regions of anomalous dispersion to be determined with much greater accuracy. It will be noticed

that the rotation at any point on this diagram is made up of the sum of abscissa and ordinate. But it will be objected that by plotting the diagram in this way, we lose the advantage of having for abscissae the percentage compositions of the various mixtures to an unknown scale. This is certainly true, but advantage so sacrificed could not at best be described as a very material one. In fact, it has no real existence whatever. The initial assumption that the rotatory powers of the constituents are unaffected by external conditions and that changes produced in the rotatory power of the mixture are due entirely to changes in its composition, is absolutely untenable. For, if it were true, then we should expect that a substance exhibiting simple rotatory dispersion, and therefore by hypothesis consisting solely of one chemical compound, would have its rotatory power unaltered by change of external conditions. This is not borne out by experiment. All active substances showing simple rotatory dispersion exhibit a change of rotation with temperature which can not be due to a change in composition in the majority of cases because the rotatory dispersion still remains simple. It is not necessary, however, because of this fact, to discard the characteristic diagram of ARMSTRONG and WALKER. It still remains true in substance provided that a change in the initial assumptions be made which involves the sacrifice of its least useful property. Instead of assuming, therefore, that the rotatory powers of the components are unaffected by external conditions, we make an assumption which is much more in accord with fact, and postulate that the dispersive powers of the components are unaffected by external conditions. This is probably quite true as far as the effect of temperature is concerned, but it may be necessary in the future to modify it when considering the effect of solvents. By changing the initial assumption, then, the theory of the characteristic diagram is placed on a much more reasonable basis, whilst the only sacrifice involved is that the abscissae now no longer represent the composition of the mixture to an unknown scale. We have thus destroyed the only advantage—a very problematical one as far as any practical use is concerned—of the ARMSTRONG-WALKER diagram over that due to PATERSON, and there seems to be no reason why the latter should not be more generally employed.

The DRUDE *Equation and the Characteristic Diagram.*

It can be shown quite readily that the deductions drawn from a consideration of the characteristic diagram are entirely in harmony with those made from the DRUDE equation.

Case I.

Substances with rotations of the same sign and with the same dispersive power.

$i.e.,\ a_0 = k_0/(\lambda^2 - \lambda_0^2):\ a_1 = k_1/(\lambda^2 - \lambda_1^2)$
but $\lambda_0 = \lambda_1$, and k_0 and k_1 have the same sign,
therefore $a = K/(\lambda^2 - \lambda_0^2)$

and the dispersion is simple.

Case II.

Substances with rotations of the same sign but with different dispersive powers.

$i.e.,\ a_0 = k_0/(\lambda^2 - \lambda_0^2):\ a_1 = k_1/(\lambda^2 - \lambda_1^2)$
but $\lambda_0 \neq \lambda_1$
and so $a = k_0/(\lambda^2 - \lambda_0^2) + k_1/(\lambda^2 - \lambda_1^2)$

and the dispersion is complex, but can not be anomalous.

Case III.

Substances with rotations of opposite sign, but with the same dispersive power.

$i.e.,\ a_0 = k_0/(\lambda^2 - \lambda_0^2):\ a_1 = k_1/(\lambda^2 - \lambda_1^2).$
but $\lambda_0 = \lambda_1$
therefore $a = C/(\lambda^2 - \lambda_0^2),$

and the dispersion is simple.

Case IV.

Substances with rotations of opposite sign, and with different dispersive powers.

$i.e.,\ a_0 = k_0/(\lambda^2 - \lambda_0^2):\ a_1 = k_1/(\lambda^2 - \lambda_1^2).$
but $\lambda_0 \neq \lambda_1$
and so $a = k_0/(\lambda^2 - \lambda_0^2) - k_1/(\lambda^2 - \lambda_1^2),$

and the dispersion is complex, and may be anomalous.

The Dispersion Ratio.

The dispersion ratio of an optically active compound is defined as the ratio of its rotatory powers for light of two arbitrarily chosen wave lengths.[44] The most convenient sources of light for this purpose are the green and violet lines of the mercury arc, which have the merit of being widely separated in the spectrum, and of being always produced together. Other colours of light are occasionally employed,[45]

chiefly the hydrogen C and F lines, but as an intense hydrogen spectrum can not be produced, an indirect method (p. 8) of illumination has to be employed, with consequent detrimental effect on the accuracy of the results.

As a scientific measurement, the dispersion ratio fails to meet the requirements of a standard, in that it is not an absolute quantity, that is to say that it involves two arbitrarily chosen wave lengths. Its interpretation may therefore be difficult, and deductions drawn with its aid may be confusing and inaccurate. For a substance exhibiting simple rotatory dispersion, however, the dispersion ratio is a useful number. We have, in this case,

$$\frac{a_{4358}}{a_{5461}} = k_0/(\cdot4358^2 - \lambda_0^2) \text{ divided by } k_0/(\cdot5461^2 - \lambda_0^2)$$

$$= \frac{\cdot5461^2 - \lambda_0^2}{\cdot4358^2 - \lambda_0^2}$$

$$= \frac{\cdot2982 - \lambda_0^2}{\cdot1899 - \lambda_0^2}$$

As λ_0 is less than λ, this fraction has its minimum value when $\lambda_0 = 0$. The dispersion ratio then becomes equal to $1\cdot570$. Any substance, therefore, of which the dispersion ratio, a_{4358}/a_{5461}, falls below this value, is certainly exhibiting complex rotatory dispersion.

Examination of Figs. 6 and 8 shows that the dispersion ratio of a substance exhibiting simple rotatory dispersion must be constant under all conditions. If, on the other hand, a substance shows complex rotatory dispersion, its dispersion ratio will not be constant although it will tend toward a constant value as the value of the rotatory power moves away from the region of intersection of the lines. This will be especially noticeable in those cases where this region is situated within two or three degrees of the line of zero rotation. The fact that this is the case for the majority of simple esters of optically active alcohols led PICKARD and KENYON to the erroneous conclusion that alcohols and their simpler esters have a common characteristic diagram.[46] It is obvious, of course, that the characteristic diagram of, for example, an alcohol with simple rotatory dispersion will be of the type shown in Fig. 8, with the lines all intersecting at one point on the axis of zero rotation, whereas that for an ester with complex rotatory dispersion will be of the type shown in Fig. 9, with the lines intersecting at different points, none of which lies on the axis of zero rotation.

It is impossible, therefore, to co-ordinate the rotatory powers of substances exhibiting simple and complex rotatory dispersion on one and the same characteristic diagram, although when, as is the case with the aliphatic esters of simple secondary alcohols, the region of intersection of the lines on the characteristic diagram is within a few degrees of the axis of zero rotation, it is very difficult to detect· the difference in form between the diagrams for the esters with complex rotatory dispersion and the alcohols with simple rotatory dispersion.

For the purpose of developing the idea of the characteristic diagram, it was assumed that complex rotatory dispersion was due to the admixture of two active substances with different dispersive powers. While this is probable in a large number of cases, it is not always necessarily true. It has been pointed out by TSCHUGAEV[47] and his pupils, that complex rotatory dispersion may be produced by the superposition of the partial rotations produced by two asymmetric centres within the same molecule, and that if these partial rotations, in addition to possessing the different dispersive powers necessary for the production of complex rotatory dispersion, also possess opposite signs, then anomalous rotatory dispersion may be produced. As an example of this is quoted *l*-menthyl β-camphorsulphonate, the two centres of activity being the menthyl and camphor radicles. This possibility must, however, be ruled out in the case of substances containing but one centre of asymmetry. Some simple cases of compounds which exhibit complex rotatory dispersion may now be considered.

The Aliphatic Esters of the Simpler Secondary Alcohols.[48]

These compounds all exhibit complex rotatory dispersion in the homogeneous state : the esters of monobasic acids at temperatures above about 30° C., and the esters of dibasic acids at temperatures even as low as 10° C. It has been suggested by SMEDLEY,[49] that the carboxylic group is better represented as

$$-C\underset{\diagdown OH}{\overset{\diagup O}{\diagdown}}\ \text{than}\ -C\underset{\diagdown OH.}{\overset{\diagup O}{\diagdown}}$$
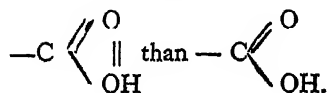
This investigator bases her opinion on a consideration of the difference between both the chemical and the physical properties conferred on a substance by the presence in the molecule of the carbonyl group in aldehydes and ketones on the one hand, and in acids, esters and amides

on the other. PICKARD and KENYON[50] and their pupils, however, have adopted this suggestion in a modified form in order to explain the complex rotatory dispersion of the majority of optically active esters. They assume that these esters consist of equilibrium mixtures of the two forms indicated by SMEDLEY, so that an ester would be represented by :—

$$R-C{\overset{\displaystyle O}{\diagup}}_{\diagdown O-R^1} \rightleftharpoons R-C{\overset{\displaystyle O}{\diagup}}_{\diagdown O-R^1} \|$$
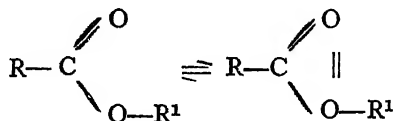
It is supposed, further that these forms have different dispersive powers and, in general, rotations of opposite sign, so that they can exhibit anomalous rotatory dispersion under the appropriate experimental conditions. When the ester exhibits simple rotatory dispersion, it is supposed that the equilibrium has gone over completely to one side or other of the above equation. Recently, however, SCHEIBLER and VOSS[51] have succeeded in preparing potassio-derivatives of esters, and they suggest the formulation of esters in such a manner that the presence of a mobile hydrogen atom is indicated. Thus, for ethyl acetate,

$$CH_3-C{\overset{\displaystyle O}{\diagup}}_{\diagdown O \cdot C_2H_5} \rightleftharpoons CH_2=C{\overset{\displaystyle OH}{\diagup}}_{\diagdown O \cdot C_2H_5}$$
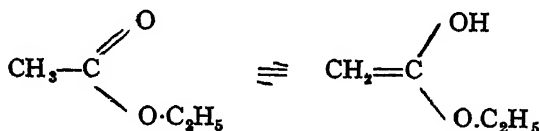
so that an alternative formulation of the isodynamic forms of these esters appears available. The fact that this is not in reality the case has, however, already been demonstrated. It will readily be seen that the formulation indicated by SCHEIBLER and VOSS necessitates the presence of a mobile hydrogen atom attached to the carbon atom immediately adjacent to the carbonyl carbon atom of the ester group. It has been shown,[52] however, that the formates of methylethyl-, methyl-n-hexyl- and ethyl-n-hexyl carbinols exhibit complex rotatory dispersion. Now the formula for a formic ester—$HC{\diagup}^{O}_{\diagdown OR}$—does not permit the mobility of the hydrogen atom attached to the carbonyl group unless the presence of divalent carbon in the molecule be assumed so that suggestion of SCHEIBLER and VOSS cannot be considered in this connection. A further proof of the inapplicability of this suggestion is to be found in the case of benzylmethylcarbinyl trimethylacetate[53]

which has been shown to exhibit complex rotatory dispersion. Here, again, there is no mobile hydrogen atom attached to the carbon atom immediately adjacent to the ester group :

$$CH_3 \diagdown \atop CH_3 —C.C \diagup\!\!\!\diagup O \atop CH_3 \diagup \qquad O.CH \diagdown \atop \diagdown CH_2\ C_6\ H_5 \quad CH_3$$
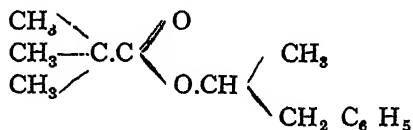
so that the suggestion of these two workers is ruled out in this case as well. It should be pointed out, however, that this case furnishes evidence which is hardly as sound as that offered by the formates, because it is quite possible that the complex rotatory dispersion of any derivative of benzylmethyl carbinol may be due to dynamic isomerism between any or all of the forms which have been suggested for the benzene ring.

Some Secondary Alcohols of More Complex Chemical Constitution.

Although the rotatory dispersions of optically active secondary alcohols of relatively simple chemical constitution obey the one term DRUDE equation, it has been shown that this is not the case for secondary alcohols with a more complicated chemical structure. The most noteworthy examples are furnished by methyl α-naphthyl carbinol[54] and *n*-hexyl α-naphthyl carbinol,[55] both of which exhibit complex rotatory dispersion at temperatures below about 160° C. In these cases it is thought that the underlying cause of the complexity of the rotatory dispersion is dynamic isomerism between the *ac-* and the *ar-* forms of the compounds, thus :—

$$CH_3.CH.OH \qquad\qquad CH_3.CH.OH$$
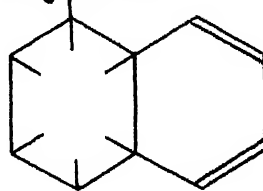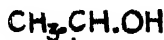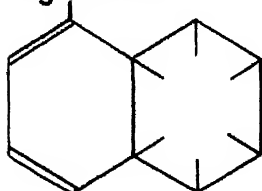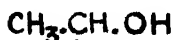
It has also been found that methylphenyl-, ethylphenyl-, methylbenzyl- and methylphenethyl-carbinols[56] show slight but distinct evidence of complex rotatory dispersion. In these cases it is probably due to dynamic isomerism between some of the various forms of the benzene

ring which have from time to time been postulated by organic chemists, some of which forms have recently been shown by INGOLD[57] and his colleagues to have a real existence. Methyl-*tert.*-butyl carbinol[58] has also been shown to exhibit complex rotatory dispersion, but no explanation of this has been put forward.

The Rotatory Dispersive Power of Compounds containing Oxygen.

Most of the substances showing complex rotatory dispersion which have been considered up to now have contained the carboxyl group or its equivalent, the carboalkyloxy group. The suggestion has been put forward that the underlying cause of this complex rotatory dispersion is the dynamic isomerism due to the variable valency of the oxygen atoms in this group. It has recently been shown that ethers[60] derived from simple active secondary alcohols exhibit simple rotatory dispersion which is, after all, to be expected, since the molecule in this case contains only one oxygen atom, which could not be expected to exercise its supplementary valencies unless some form of association were to occur, and it is known that this is not the case. More recently still, it has been shown[61] that di-ethers (*sec.*-octyl formal), carbonates, *sec.*-octyl orthoformate and *sec.*-octyl sulphite all exhibit simple rotatory dispersion, at least under the experimental conditions hitherto attained. These compounds are alike amongst themselves and also resemble the esters in that they contain more than one oxygen atom in the molecule, thus :—

$$H_2C \big\langle \begin{array}{l} O.C_8H_{17} \\ O.C_8H_{17} \end{array}$$

di-*sec.*-octyl formal

$$HC \begin{array}{l} O.C_8H_{17} \\ -\ O.C_8H_{17} \\ O.C_8H_{17} \end{array}$$

tri-*sec.*-octyl orthoformate

$$O{=}C \big\langle \begin{array}{l} O.C_8H_{17} \\ O.C_8H_{17} \end{array}$$

di-*sec.*-octyl carbonate

$$O{=}C \big\langle \begin{array}{l} O.C_2H_5 \\ O.C_8H_{17} \end{array}$$

sec.-octyl ethyl carbonate

$$O{=}S \big\langle \begin{array}{l} O.C_8H_{17} \\ O.C_8H_{17} \end{array}$$

di-*sec.*-octyl sulphite
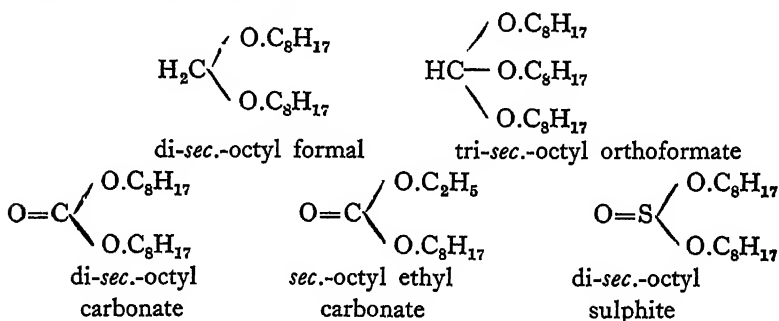
Here, however, the resemblance ends. In the case of the formal and the orthoformate, the oxygen atoms in the molecule are all ethereal in character and it may be assumed that there will therefore be no tendency for them to exercise their quadrivalancy. There will thus be no dynamic isomerism with the result that the rotatory dispersion of the compounds will be simple. In the case of the carbonates and

the sulphite, however, there is on the one hand a carbonyl oxygen atom, and on the other hand a sulphinic oxygen atom, both of which might be expected to exercise supplementary valencies with the remaining oxygen atoms in the molecule. It will be seen, however, that these remaining oxygen atoms are symmetrically disposed about the active one, so that, having an equal choice of partners, so to speak, it pairs with neither and an essentially static form of molecule results, with consequent simplicity of rotatory dispersion.

Considerable support is afforded to this view by the fact that the nitrites of these secondary alcohols with simple rotatory dispersion, exhibit complex, and sometimes even anomalous,[62] rotatory dispersion. This is precisely what would be expected from the preceding cases, for in the nitrites we have exactly the conditions requisite for complex rotatory dispersion of oxygen compounds, namely, a doubly-linked oxygen atom present in the same molecule with another oxygen atom unsymmetrically placed with respect to the first, thus :—

$$\underset{R\,-\,O\,-\,N}{\overset{\overset{O}{\|}}{}} \quad \rightleftharpoons \quad \underset{R\,-\,O\,-\,N}{\overset{\overset{O}{\|}}{/\!/}}$$

Static Isomerism and Complex Rotatory Dispersion.

One of the consequences of improvements in chemical technique is that the dynamic isomerism of to-day becomes the static isomerism of to-morrow. Having postulated the existence of dynamic isomerides in liquids showing complex rotatory dispersion, it was only natural that chemists should seek some method of arresting the interconversion of the isomerides in order to be able to separate them. This separation has actually been achieved in some cases, notably those of glucose,[63] lactose,[64] nitro-,[65] chloro-[66] and bromo-camphor.[67] In all these cases it is found, naturally, that mutarotation occurs in the fresh solutions of both isomerides, each of which ultimately attains the rotation value of the equilibrium mixture. It is found, too, that these isomerides exhibit simple rotatory dispersion. In some cases, for example glucose, the dispersive powers of the isomerides are the same, with the result that the equilibrium mixture also exhibits simple rotatory dispersion. In other cases, for instance, α-chlorocamphor, the dispersive powers of the different isomerides are not the same, so that the dispersive power of the equilibrium mixture of the simply dispersing components is complex.

Dynamic Isomerism and Crystal Structure.

Quite recently, the crystal structure of *d*-tartaric acid has been determined by ASTBURY,[68] who finds within the crystal unit two spiral arrangements which are differently handed but not mirror-image complements. One of these spirals is associated with the four carbon atoms in the molecule and is said to persist even in solution. The other spiral is associated with the four hydroxyl groups in the molecule, and is said to disappear in solution. It is claimed that the presence of these two spirals is sufficient to account for the complex rotatory dispersion of tartaric acid and that " the involved explanation suggested by LOWRY is thus unnecessary."[69] It is rather premature to discuss these results till more evidence is available to support the interpretation which has been placed upon them, but two pertinent questions are suggested immediately. The first is : if one of the spirals is destroyed by solution, how can its presence affect the dispersion of the solution ? The second is : if both spirals are present in solution (in order to reply to the first question) how is the simple rotatory dispersion of sodium tartrate to be accounted for ?

V.

This subject has been developed almost entirely by the efforts of
PATTERSON and his pupils. The investigation dates from about
1901,[70] although the question of dispersion was not considered till
very much later. Certain aspects of the earlier work, however, must
be considered, as they influence to a certain extent the later investiga-
tions. A good deal of the work was done with esters of tartaric acid,
particularly ethyl tartrate, a somewhat unfortunate choice, perhaps,
for this ester contains two asymmetric carbon atoms in the molecule,
exhibits anomalous rotatory dispersion in the visible spectrum and
may possibly be a mixture of dynamic isomerides.

Rotatory Power and Solution Pressure.

An investigation of the variation of the rotatory power of ethyl
tartrate in the solvents, water, methyl, ethyl and *n*-propyl alcohols
showed certain regularities to exist,[71] and consequently, PATTERSON
endeavoured to connect rotatory power with internal solution pressure.
Briefly, his argument is as follows :—

Suppose a molecule of ethyl tartrate to be taken from a large number
of similar molecules and placed amongst a large number of water mole-
cules. The pressure on the molecule will then change from the value
which it has in ethyl tartrate to that which it has in water. Associated
with change in pressure we generally find change in volume—and,
if the molecule be anisotropic, we shall also find change of shape,
with consequent change in asymmetry and in rotatory power. The
molecular solution volume (M. S. V.) of a substance in solution is
measured by :—

$$\text{M. S. V.} = \frac{M}{p}\left(\frac{100}{d} - \frac{100-p}{D}\right)$$

where M = molecular weight of the substance,
      p = the percentage of solute in the solution,
      d = density of the solution,
      D = density of the solvent.

By comparing the rotatory power of ethyl tartrate in various solvents at infinite dilution with its M. S. V. in the same solvents at infinite dilution, PATTERSON established a qualitative, but not a quantitative relationship between these two properties. On extending this work to other solvents he was forced, in 1908, practically to abandon this idea[72] because the exceptions had become so numerous and important. It should be pointed out, however, that his results were not free from the effects of temperature and dispersion.

In 1904,[73] he investigated the temperature-rotation curves for methyl, ethyl and n–propyl tartrates in the homogeneous state. He found no simple relationship between the rotatory powers of the homologues at any temperature, and was then led to compare their rotatory powers at " corresponding " temperatures. By extrapolation of the temperature-rotation curves to $[M]_D = 0°$, he found for methyl tartrate that $t = 0°C.$, for the ethyl ester that $t = —84° C.$, and for the n-propyl ester that $t = —60° C.$ He therefore proposed a comparison of rotatory powers at $T°$, $T—34°$, and $T—60° C.$ for the three esters, respectively. From his results he found that, at corresponding temperatures, $[M]_D$ for n-propyl tartrate was $1·4$ times that for ethyl tartrate, which was in turn twice that for methyl tartrate.

Having practically abandoned the idea of connecting rotatory power with internal solution pressure, PATTERSON gave up the deductive method in favour of the inductive. Examination of the effect on rotatory power of many more solvents enabled him to propound the following hypotheses[74] :—

(a) If a solvent exalts the rotatory power of an active body, then rise of temperature depresses the rotatory power of the solution, and conversely.

(b) The course of the temperature-rotation curve at any point is apparently defined by the rotation at that point.

Hence he proceeded to another generalisation. Consider, for example, an optically active body dissolved in a liquid which exalts its rotatory power, for instance, ethyl tartrate in nitrobenzene (Fig. 14). The maximum in the temperature-rotation curve is obviously moving towards a higher value of the rotation with a lower value for the temperature with increasing dilution. Then there will be a particular concentration for which the maximum rotation lies between, say, 20° and 100° C.,

and for which $[\alpha]_D^{20°} == [\alpha]_D^{100°}$. Let this maximum rotation be $x°$. Then it is found that :—

$$k\left(X - [\alpha]_D^{20°}\right) = [\alpha]_D^{100°} - [\alpha]_D^{20°} \quad *$$

The constants k and X can be found by considering a number of experimental figures and are found to be to a certain extent independent of the
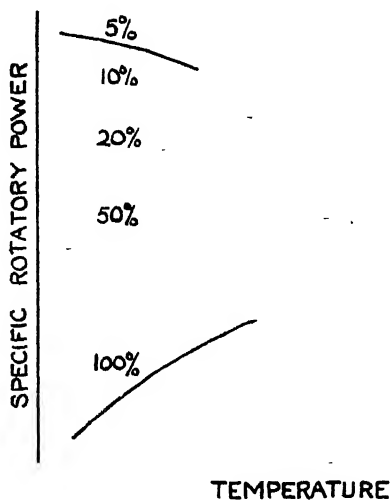
FIG. 14.

solvent. There are again, however, numerous and important exceptions.

Then, in 1913, PATTERSON put forward a suggestion which[75] was to "harmonise, qualitatively, the relation between temperature and rotation for light of all refrangibilities, of certain active substances, both in the homogeneous state and in solution."

The suggestion is that the temperature-rotation curve for any active body is periodic in character, but variable in period, amplitude, and

* The fallacy of this equation is apparent on a little consideration. At the risk of elaborating the obvious, it may be pointed out that it cannot apply to the simple case considered above.

For if $[\alpha]_D^{20°} = [\alpha]_D^{100°}$

then the right hand side of the equation becomes equal to zero, that is either
$$k = 0, \text{ or } X° = [\alpha]_D^{20°}$$
both of which conditions are absurd.

phase. As a first approximation, " mainly as a concrete example and for purposes of illustration," he proposes an equation of the form :—

$$a = e^{-at} \sin (b t + c)$$

where ' a ' is the parameter of amplitude, ' b ' of period, and ' c ' of phase.

There are three obvious objections to this expression. First, no physical significance can be assigned to the sine of a temperature. Second, the exponential term e^{-at} is in itself suspicious. The exponential equation is beloved of the empiricist because it may be made to fit so many experimental results. But the fact that it can be made to fit a given set of figures is no guarantee that it is the correct equation to apply—no theoretical deductions whatever can be drawn from its use. It is a tower of strength to the engineer who frankly admits his ignorance of the nature of the function with which he is dealing, and who uses the equation only as a means of interpolation between his experimental results. This is its legitimate sphere (unless of course, there is other evidence that the function really is an exponential one), and it is utterly useless as a method of extrapolation. Indeed, unless it is very guardedly employed, it may become a source of positive danger because it tends to assume a spurious appearance of scientific accuracy, and may, therefore, be accepted as a natural " law " by the unwary. The third objection is more of a practical nature. The temperature-rotation curves for very many substances are very nearly linear over a temperature range of nearly 200° C.[76] The period of a sine curve of the above type must be very large in order to accommodate a linear curve for this great temperature range. This objection alone robs PATTERSON'S suggestion of most of its claim to be regarded as a valuable contribution to our knowledge of the subject.

But he proceeds to develop his hypothesis still further. Having decided on his fundamental temperature-rotation curve, he assumes that the effect of some solvents is to bring hitherto inaccessible portions of the curve into the region of experimental observation. Still bolder, he imagines that a family of chemical compounds has one fundamental temperature-rotation curve—the curve, so to speak, of the parent substance—and that the derivatives of this parent compound have temperature-rotation curves which form part of the fundamental one. Further, the greater the difference between the chemical constitutions of the parent compound and the derivative, the farther apart will

be their observed temperature-rotation curves on the fundamental one.

Thus, in Fig. 15, the portion of the curve *c d e f g h* represents the experimentally determined temperature-rotation curve for ethyl tartrate in the homogeneous state. Solution in a liquid which does not bring about much change of rotation gives a curve very similar to *c d e f g h*. If the solvent, however, has a powerful elevating effect on the rotation, the shape of the curve gradually alters as the concentration of the active substance diminishes, starting, of course, from that for the homogeneous compound, passing through the form *e f g h i*
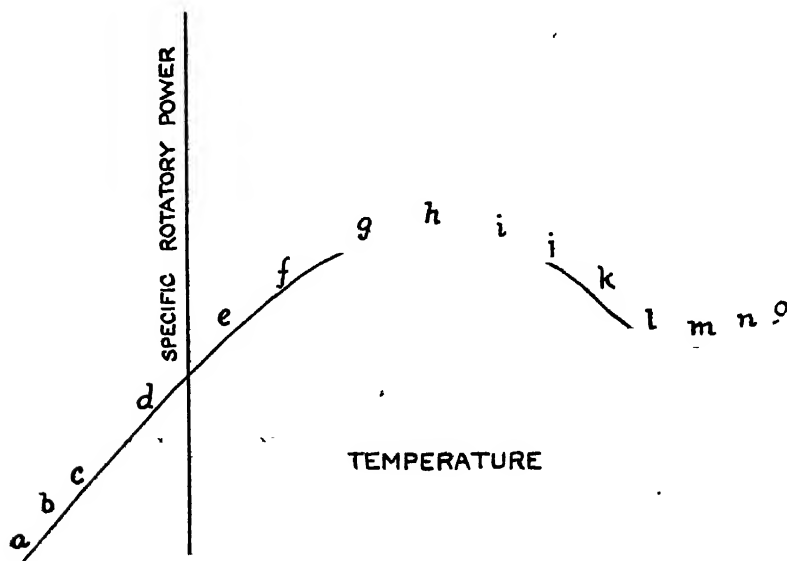
FIG. 15.

to *g h i k* in the most dilute solutions. With a solvent which has a still more powerful influence on rotatory power, it might even be possible to realise the portion *k l m n o* of the curve. A solvent with a depressing effect on the rotation, will, on the other hand, bring into view the portion *a b c*, and so on. Change in the constitution of the active body, too, is supposed to have a somewhat similar effect. A small change say to *iso*butyl tartrate, brings into view the portion of the curve *f g h i k*, whilst a greater change to, say, *iso*butyl diacetyl-tartrate, has a greater effect, and brings into view the portion *l m n o*.

So far, light of one wave length only has been considered. PATTERSON considers that the temperature-rotation curves for light of other wave lengths are similar ones which, however, differ considerably in amplitude, and sometimes also slightly in period and in phase.[77] He then points out that anomalous rotatory dispersion occurs when the temperature-rotation curves for light of different refrangibilities are displaced slightly in phase, so that they do not intersect at one point.

It must be confessed, however, that this " sine curve " theory has very little to recommend it. Not only does it fail to co-ordinate the observed experimental facts, but it also requires a good deal of faith for its acceptance even when limited in its application to very few compounds. The periodicity pointed out by PATTERSON is very difficult to observe even in his own results : no trace of it is to be found in the results obtained by other investigators. The practice of extending, for example, the temperature-rotation curve for a substance in the homogeneous conditions by grafting on to it the temperature-rotation curve for the same substance in some solvent is entirely indefensible ; more, it is impracticable. There is no guarantee that the scales of temperature and rotation respectively are the same in each case. Furthermore, it can be shown that closely related compounds do not always have similar temperature-rotation curves. d-*sec*. octyl formate[78] and acetate[79] form a case in point. The former compound has not been observed to exhibit anomalous rotatory dispersion in the visible region of the spectrum, but consideration of its temperature-rotation curves for light of different wave lengths shows that it may do so at a temperature in the neighbourhood of — 50° C. d-*sec*. octyl acetate, on the other hand, has been observed to show anomalous rotatory dispersion in the visible spectrum in the homogeneous state at a temperature of about 160° C. That is to say, that the change in constitution produced by proceeding from the formate to its next higher homologue has caused the point of intersection of the temperature-rotation curves for light in the visible region of the spectrum to move over a temperature range of about 200° C.

For the purpose of this discussion, however, the chief interest of PATTERSON'S work lies in two papers published in 1916.[80] In these papers he puts forward some views of his own on the subject of rotatory dispersion, and criticises those supported by other workers.

The Rational Zero.

" In the early days of optical activity it was supposed that the specific rotation of a compound would be a genuine constant independent

of external conditions, and although this expectation was grievously disappointed, there still exists a hope that dispersive power may prove to be sufficiently independent of external conditions to serve for the definite characterisation of the substance to which it pertains."[81]

This idea underlies the first of these papers. PATTERSON, of course, uses a dispersion ratio as a measure of dispersive power. But he finds, as indeed every worker in this field has found, that dispersion ratios are by no means independent of external conditions in every case. Instead of accepting this fact, however, and endeavouring to determine the conditions under which dispersion ratios *are* constant, he sets out to find a way of calculating dispersion ratios in order to *make* them constant. He says that :—

" The dispersive power, in order really to be useful, must remain constant, or at least approximately so, with varying circumstances, and not have arbitrary normality or anomalousness (*sic*) in accordance with purely accidental circumstances, such as a very slight change of temperature, or solvent, or concentration."[82]

The wisdom of this statement is very much open to question. There is very little merit or use in constancy *qua* constancy : that is, a constant is useful only when we know what it means, for only then can a meaning be assigned to any particular deviation. Now no meaning can be assigned to a dispersion ratio—it is entirely arbitrary. It is true, of course, that the ratio is constant for substances exhibiting simple rotatory dispersion, but for those with complex, and especially for those with anomalous rotatory dispersion it can, and does, assume many values. However, PATTERSON, having decided that dispersion ratios are not sufficiently constant for his purpose, proceeds to calculate them anew with a view to the introduction of the necessary constancy. To do this, he introduces the new conception of the " rational zero." From a consideration of various temperature-rotation curves and characteristic diagrams, he comes to the conclusion that the zero of the polarimeter has little or no physical significance, and proposes to substitute for it the rational zero, which is the rotatory power of the particular substance under consideration at which the temperature-rotation curves for the two particular wave lengths intersect. Or, what amounts to the same thing, it is the value of the rotatory power for the particular substance under consideration at which the lines on the characteristic diagram for these two wave lengths intersect. Then, as PATTERSON points out, if this point be regarded as the zero of rotation, dispersion ratios calculated from it are found to be much more

constant than if calculated in the usual way from the physical zero of the polarimeter. Of course they are : provided that the lines on the characteristic diagram are straight, which is very often found to be the case, it follows that this suggestion is merely a piece of geometrical legerdemain in which the properties of similar triangles are employed to obscure the real scientific issue. The announcement of the fact that the use of the rational zero imparts constancy to the dispersion ratio is thus the rediscovery in a particular form of facts which have been known to science for at least two thousand years. But the main objection to the proposal is far more serious. PATTERSON cannot be unaware of the fact that there are two kinds of characteristic diagram —those in which all the lines intersect in one point, the zero of rotation, and those in which the lines do not intersect in one point. These two types correspond to substances with simple and complex rotatory dispersion, respectively. Furthermore, it follows from the DRUDE equation with two terms that in characteristic diagrams of the second type, no more than two lines can intersect at one point, and no two lines can intersect on the axis of zero rotation. Therefore, for substances of the second-class, PATTERSON'S suggestion leads logically to the postulation of an infinite number of rational zeros, depending on which particular two of the infinite number of wave lengths at his disposal he chooses for the calculation of the dispersion ratio. And all this for one substance only : for any other, the rational zeros will be different. Even if the validity of the DRUDE equation be not admitted, we cannot get away from the undoubted experimental fact that substances *do* exist, for which the lines on the characteristic diagram do not all intersect at one point, and for which, therefore, a large number of rational zeros would be required. The conception of the rational zero, then, must be dismissed as unworthy of further consideration ; it was designed for a purpose which has been shown to be unscientific, and its adoption leads to a labyrinth of arithmetical computation from which there is no escape.

In the second of these papers, PATTERSON criticises the DRUDE equation and the conception of dynamic isomerism as an explanation of the phenomenon of anomalous rotatory dispersion. His objections to the DRUDE equation are twofold. He says that it " is based on very hypothetical grounds, and is already gravely suspect by reason of the fact that it ignores the influence of temperature on rotation."[83] The first objection is very easily met. The electronic theory of light, like many other theories, is certainly hypothetical, but its success in

correlating the very varied phenomena of optics is such that' it will require much more than mere assertion to shake it. His second objection is ingenuous in the extreme. The DRUDE equation certainly ignores the effect of temperature on rotation. It is a dispersion equation, pure and simple, and does not pretend to deal with temperature effects. It is tacitly assumed, naturally, that rotations for different wave lengths are to be compared at one and the same temperature. Would PATTERSON seriously assert, for instance, that BOYLE'S law " is already gravely suspect " because " it ignores the influence of temperature " on pressure or volume ? Yet the two cases are exactly similar. Just as BOYLE'S law was extended to include the influence of temperature by the discovery of the law of CHARLES, and the combined equation was modified subsequently by VAN DER WAALS to introduce the effects of the mutual attractions and the volumes of the molecules, so, it is hoped, will the rotation constants and dispersion constants of the DRUDE equation be modified to express the effect of change of temperature and of solvent. For the present, however, this is merely an aspiration ; much more work must be done before the effect of experimental conditions on the constants of the DRUDE equation is even dimly understood ; for the time being we must be content with the knowledge that the modifications we seek must surely be found because the search is being conducted in a logical manner.

PATTERSON does not approve of the postulation of dynamic isomerism in order to explain anomalous dispersion, and here, perhaps, his attitude is understandable. A dynamic isomeride of a compound is essentially one which cannot be isolated and put into a bottle. Postulation of the existence of such isomerides immediately denies an opponent the right of challenging one to produce the compounds duly labelled and analysed. But to ignore the fact that dynamic isomerism does occur in many cases known to chemists is hardly scientific. It is known, too, ·that labile isomerism is sometimes accompanied by complex rotatory dispersion, and further, in those cases where complex rotatory dispersion has been observed, the occurrence of dynamic isomerism is certainly not improbable, and in many of the cases it has been shown purely on chemical grounds to be highly probable. The following, which seems to the writer to be the really important objection to this hypothesis, is not, however, mentioned by PATTERSON. It is difficult to understand why a very slight change in constitution—often merely the redistribution of the valency forces amongst three or four of the atoms in the molecule—should have in some cases such an

enormous effect on the optical properties of the molecule as not only to cause its rotatory power to change sign, but also to alter the value of its rotatory dispersive power.

But the fact remains that the DRUDE equation forms what is at present the only means of explaining anomalous rotatory dispersion —its nature and under what conditions it may occur. It is not merely the most accurate formula extant—it is the only one. Its opponents have not yet proposed a substitute ; they are at present in the vague stage and are content with statements such as " the potentialities of the asymmetric carbon atom and of the most simple physical con-ception of those intermolecular forces to which liquifaction is due, are ample to account for all the observed behaviour," [84]—and the like.

It is somewhat unfortunate, perhaps, that of all the causes which may give rise to a two term DRUDE equation, and hence to complex and possibly anomalous rotatory dispersion, dynamic isomerism has been singled out almost to the exclusion of the others. It must not be forgotten that for complex rotatory dispersion to occur, all that is necessary in the medium is the presence of two rotatory elec-trons of different period. We are not compelled even to assume that these electrons exist in different molecules, much less that the different molecules are dynamic isomerides. Association, dissociation, solvate formation, and the superposition of the partial rotations produced by different asymmetric complexes within the same molecule may also be causes giving rise to optical non-homogeneity such as determines complexity of rotatory dispersion. The fact remains, too, that by means of these phenomena we are able to explain with remarkable success the varied aspects of rotatory dispersion. It is true, of course, that the hypotheses are incapable of direct proof, or even, at present, of direct experimental test, but it is maintained that they are not inconsistent with facts observed in other branches of chemical science, and that they provide what is at present the only satisfactory explanation of the facts of rotatory dispersion.

VI.

THE CHEMICAL SIGNIFICANCE OF ROTATORY DISPERSION.

Consideration has already been accorded to the views of two schools
of thought upon the chemical significance of rotatory dispersion.
LOWRY and his co-workers together with ARMSTRONG and his
pupils, incline to the belief that, in the majority of cases, dynamic
isomerism is the cause of the optical heterogeneity leading to complex
dispersion. In this view they have been followed, not very whole-
heartedly perhaps, by PICKARD and KENYON and their students.
PATTERSON, on the other hand, will have nothing whatever to
do with this hypothesis. It now becomes necessary to take up a definite
standpoint with regard to the two theories. It has been shown that
PATTERSON'S position is practically untenable—it needs far too
many assumptions and, even then, suggests no new lines of research.
LOWRY'S views are more plausible—let us examine them more
closely.

In the first place, as has already been pointed out, the DRUDE
equation was obtained from fundamental assumptions which have
nothing whatever to do with dynamic isomerism ; that is a develop-
ment which came later. This dispersion equation is concerned only
with the oscillation frequencies of the asymmetric vibrators within
the molecule or other absorbing system—other ideas are extraneous
to the theory. Putting these ideas on one side for the time being,
then, let us examine the consequences of this theory of rotatory dis-
persion. To begin with, it is to be expected that simple rotatory
dispersion would be a very rare phenomenon. All the evidence of
absorption spectroscopy goes to show that a compound with only one
band in its absorption spectrum does not exist. Whilst it must be ad-
mitted that not all of the absorption bands exhibited by any com-
pound will affect the rotatory dispersion (though they must all influence
the refractive dispersion), yet it seems improbable that any substance
can exist which exhibits one, and only one, rotatory absorption band.
But LOWRY has emphasised the fact that simple dispersion is the
rule, complex dispersion the exception, amongst organic compounds.

In order to understand the reason for this discrepancy, it is necessary to examine the method of distinguishing between simple and complex rotatory dispersion. This method is based on the fact that the one term DRUDE equation is linear in $1/a$ and λ^2. For if

$$a = \frac{k_0}{\lambda^2 - \lambda_0^2}$$

then

$$\frac{1}{a} = \frac{1}{k_0}\lambda^2 - \frac{\lambda_0^2}{k_0}$$

The two term equation, however, is not linear in these variables. Therefore it would appear that the graphical method of plotting $\dfrac{1}{a}$ against λ^2 would differentiate between the two forms of dispersion. This method has already been suggested by LOWRY and DICKSON.[95] But a closer examination of the two term equation will reveal the fact that the method is unsound.

Consider the equation :—

$$a = \frac{k_0}{\lambda^2 - \lambda_0^2} + \frac{k_1}{\lambda^2 - \lambda_1^2}$$

then

$$\frac{1}{a} = \frac{\lambda^4 - \lambda^2(\lambda_0^2 + \lambda_1^2) + \lambda_0^2\lambda_1^2}{\lambda^2(k_0 + k_1) - k_0\lambda_1^2 - k_1\lambda_0^2}$$

Putting $\dfrac{1}{a} = y$; $\lambda^2 = x$; $(\lambda_0^2 + \lambda_1^2) = a$; $\lambda_0^2\lambda_1^2 = b$;

$k_0 + k_1 = c$; and $k_0\lambda_1^2 + k_1\lambda_0^2 = d$

we get $y = \dfrac{x^2 - ax + b}{cx - d}$

which may be written in the form :—

$$y = \frac{x}{c} + \frac{d - ac}{c^2} + \frac{b + \dfrac{d^2 - acd}{c^2}}{cx - d}$$

which is the equation to a hyperbola. By inspection, it follows that :—

(a) y is infinite only when the third term is infinite, i.e., when

$$cx - d = 0, \text{ or } x = \frac{d}{c}$$

and

(b) the equation is linear in x when the third term is zero, *i.e.*, when

(i.) $b = \dfrac{a\,c\,d - d^2}{c^2}$

or (ii.) $c\,x - d$ is infinite.

Taking these conditions in turn, we find that

(a) $\dfrac{1}{a}$ is infinite (or $a = 0$) when

$$\lambda^2 = \frac{k_0 \lambda_1^2 + k_1 \lambda_0^2}{k_0 + k_1}$$

(b) the expression is linear in $\dfrac{1}{a}$ and λ^2 when

(i.) $\lambda_0^2 \lambda_1^2 = \dfrac{(\lambda_0^2 + \lambda_1^2)(k_0 + k_1)(k_0 \lambda_1^2 + k_1 \lambda_0^2) - (k_0 \lambda_1^2 + k_1 \lambda_0^2)^2}{(k_0 + k_1)^2}$

which is satisfied if, and only if, $\lambda_0 = \lambda_1$ and

(ii.) $(k_0 + k_1)\lambda^2 - (k_0 \lambda_1^2 + k_1 \lambda_0^2)$ is infinite, *i.e.*, when λ^2 is infinite.

The asymptotes to the hyperbola are :—

(a) $\lambda^2 = \dfrac{k_0 \lambda_1^2 + k_1 \lambda_0^2}{k_0 + k_1}$ and

(b) $\dfrac{1}{a} = \dfrac{\lambda^2}{k_0 + k_1} + \dfrac{k_0 \lambda_1^2 + k_1 \lambda_0^2 - (\lambda_0^2 + \lambda_1^2)(k_0 + k_1)}{(k_0 + k_1)^2}$

These reciprocal rotation curves are plotted in Figs. 14-19, and four cases are distinguished just as in Figs. 1-4, to which these reciprocal curves exactly correspond.

It follows at once that this graphical method is one which gives its most sensitive indications when the dispersion is anomalous in or near the visible region of the spectrum. It should, however, differentiate, between simple, and all cases of complex rotatory dispersion, provided only that measurements can be carried out over a sufficiently extended region of the spectrum. It is obvious, both from the foregoing and from the figures, that $\dfrac{1}{a}$ becomes infinite whenever a becomes equal to zero. This condition enables us immediately to fix the position of one of the asymptotes to the $\dfrac{1}{a} \big/ \lambda^2$ curve for all four cases.

Case I.

$a = k_0 / (\lambda^2 - \lambda_0^2)$. a never assumes a zero value for a finite value of λ and the $\dfrac{1}{a} \Big/ \lambda^2$ curve is linear, cutting the axis of λ^2 where $\lambda^2 = \lambda_0^2$.

FIG. 16.

FIG. 17.

$a = 1/(\lambda^2 - 0.09)$

$a = 1/(\lambda^2 - 0.09) + 1/(\lambda^2 - 0.04)$

$a = 2/(\lambda^2 - 0.09) - 1/(\lambda^2 - 0.04)$
$K_0 > k_1 . \lambda_0 > \lambda_1$

$a = 1/(\lambda^2 - 0.09) - 2/(\lambda^2 - 0.04)$
$k_0 < k_1 : \lambda_0 > \lambda_1$
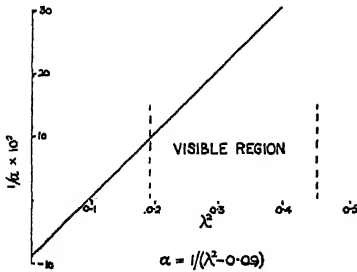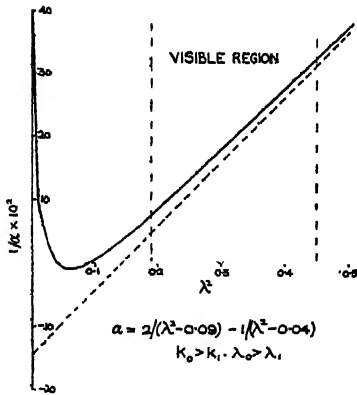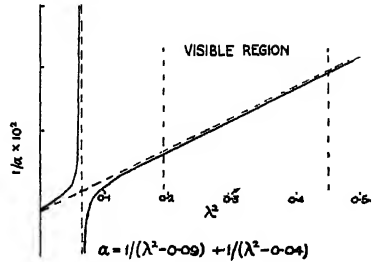
FIG. 18.
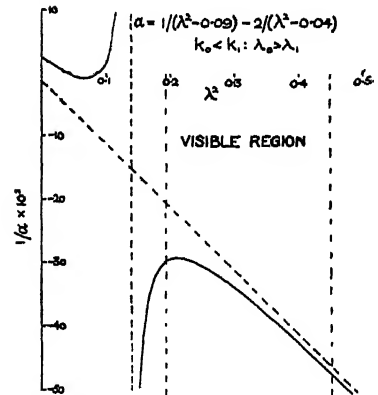
FIG. 19.

Case II.

$a = k_0 / (\lambda^2 - \lambda_0^2) + k_1 / (\lambda^2 - \lambda_1^2)$. In this case the dispersion cannot become anomalous for any value of λ greater than the wave length of the rotatory absorption band of greater wave length. $a = 0$, and $\dfrac{1}{a} = \infty$ for a value of λ intermediate between λ_0 and λ_1.

Case III.

$a = k_0/(\lambda^2 - \lambda_0^2) - k_1/(\lambda^2 - \lambda_1^2)$, and $k_0 \succ k_1$ when $\lambda_0 \succ \lambda_1$. In this case the dispersion can not become anomalous for any value of λ greater than the wave length of the absorption band of shorter wave length. $a = 0$, and $\dfrac{1}{a} = \infty$ for a value of λ less than λ_1.

Case IV.

$a = k_0/(\lambda^2 - \lambda_0^2) - k_1/(\lambda^2 - \lambda_1^2)$, and $k_0 \prec k_1$ when $\lambda_0 \succ \lambda_1$. This is the only case in which anomalous dispersion can occur for values of λ greater than the wave length of the rotatory absorption band of greater wave length. $a = 0$, and $\dfrac{1}{a} = \infty$ for a value of λ which may lie in, or very near to, the region of experimental measurement.

It appears, then, that the main factor governing the departure of these reciprocal rotation curves from linearity is the position of the asymptote $\lambda^2 = \dfrac{k_0 \lambda_1^2 + k_1 \lambda_0^2}{k_0 + k_1}$ and it follows at once that this curvature can be detected with certainty only in Case IV. In the other cases, the departure from linearity becomes noticeable only in regions close to an absorption band ; nearly always in positions where the absorptive power of the substance itself renders polarimetry impossible.

It is submitted, therefore, that this graphical method of plotting $\dfrac{1}{a}$ against λ^2 does not distinguish between simple and complex rotatory dispersion but rather between normal and anomalous dispersion—if by the term " anomalous " we mean " becoming anomalous for some values of λ greater than the wave length of the less refrangible rotatory absorption band in the ultra-violet."

Now, of course, the apparent preponderance of substances exhibiting simple rotatory dispersion can be understood. Although it is not denied that substances may exist which show simple rotatory dispersion, we must not lose sight of the fact that a complex dispersion may simulate simplicity so closely that its true character escapes detection. It is, therefore, not improbable that most, if not all, of the compounds which have hitherto been considered to exhibit simple rotatory dispersion really show complex dispersion. The number

of apparently homogeneous substances exhibiting obviously complex rotatory dispersion is relatively small, and, up to the present, the postulation of the existence of dynamic isomerism of various types has sufficed to account for the optical heterogeneity of which the complex dispersion is symptomatic. If, however, the existence of dynamic isomerism is postulated in order to explain Case IV., we are logically bound to admit it in Cases II. and III. Sooner or later, therefore, we may have to extend very considerably the list of substances suspected of exhibiting dynamic isomerism, and we may be led to an impasse where chemical evidence conflicts with physical ideas. This possibility is by no means a remote one. We have already (p. 48) noted the case of methyl *tert.* butyl carbinol which shows distinct signs of complexity of rotatory dispersion. More recently, a series of ethers of optically active ethyl *n*-hexyl carbinol has been described, the members of which undoubtedly show complex rotatory dispersion. In none of these cases can we find a plausible chemical basis for the existence of dynamic isomerism, or indeed any evidence of chemical heterogeneity.

The conclusion is inevitable, therefore, that dynamic isomerism is by no means the only cause of complex rotatory dispersion in chemical compounds of simple structure. It may be, and possibly is, the cause in a few cases, but these are not sufficiently numerous to form the basis of a chemical classification on optical grounds. There is no evidence that simple rotatory dispersion ever exists, and, whilst there seems to be a chemical distinction between those compounds with dispersive powers falling under Case IV. and those whose dispersive powers fall under Cases I., II. and III., our knowledge is at present too indefinite to enable us to formulate a theory. It will be seen that this amounts to a statement that we have returned to the older classification of dispersion into " normal " and " anomalous."

The case of tartaric acid and its derivatives is of particular interest in this connection. LOWRY and AUSTIN claim to have isolated " fixed " derivatives of tartaric acid—derivatives of one labile isomeric form only. They base their claim on the following grounds. Tartaric acid, its esters, and its alkali salts all exhibit complex rotatory dispersion. Aqueous solutions of tartar emetic, however, apparently exhibit simple rotatory dispersion between λ 6708 and λ 8984 and all these solutions are strongly dextro-rotatory. Similarly, aqueous solutions of tartaric acid in the presence of excess of boric acid are laevo-rotatory and appear to exhibit simple rotatory dispersion between λ 6708 and

λ 4100. These investigators assume, therefore, that tartar emetic is a fixed derivative of the simply dispersing destro-rotatory labile isomer, and that borotartaric acid is a fixed derivative of the simply dispersing laevo-rotatory labile isomer. They therefore consider that the results obtained with tartaric acid and its derivatives furnish very strong evidence in support of the view that dynamic isomerism, in this case at least, is the cause of the complex rotatory dispersion, and that the optical behaviour of tartrates is capable of a simple chemical explanation.

These conclusions are very much open to criticism. Firstly, no significance can be attached to the sign of the rotation. The many cases of the WALDEN inversion show that sign of rotation is no clue to sign of molecular configuration. This conclusion also follows from the work done on the structure of the sugars. It can also be shown by the examination of much simpler compounds. *sec.*-Octyl alcohol, in its destro-rotatory form, gives a laevo-rotatory formate, sulphite and chloride, from which the dextro-rotatory alcohol may be regenerated by hydrolysis. Similarly, all the aliphatic esters of ethyl *n*-hexyl carbinol have rotatory powers opposite in sign to that of the parent alcohol. If these are to be regarded as " fixed " derivatives of the alcohols, it must follow that the alcohols themselves exist in two labile forms. Secondly, the dispersion constants of tartar emetic and borotartaric acid are given by LOWRY and AUSTIN as $\lambda_0^2 = 0.049$ and 0.024 microns squared, respectively, whilst those for tartaric acid are given as $\lambda_0^2 = 0.074$ and $\lambda_1^2 = 0.08$ microns squared. If the antimonyl-and boro-derivatives of the acid represent true " fixed " derivatives of the different labile forms of the acid, one should have $\lambda_0^2 = 0.074$ and the other should have $\lambda_0^2 = 0.08$. The fact

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* It should be pointed out, however, that these investigators have omitted to carry out some very important confirmatory experiments with regard to borotartaric acid. They have adduced no evidence, beyond that afforded by dispersion measurements, that borotartaric acid exists in solutions of boric and tartaric acids. Tartaric acid is stronger than acetic acid—its first dissociation constant is $k = 1 \times 10^{-3}$. Boric acid is very weak, with a dissociation constant of 6×10^{-10}. Electrometric determinations of the hydrogen ion concentration of a solution of tartaric acid to which successive quantities of boric acid are added should, therefore, reveal whether or not combination is occurring and also when, if ever, the tartaric acid is completely transformed into borotartaric acid. Conductivity measurements should lead to similar results, although both these methods will fail in the unlikely event of borotartaric acid being of exactly the same strength as tartaric acid. It can be shown quite readily that for the case of simple mixture of the two acids, the hydrogen ion concentration of the solution will not change on the addition of boric acid, whilst if combination occurs, the curve obtained by plotting

that tartar emetic has $\lambda_0^2 = 0\cdot049$ goes to show that it is an example of Case II. with an apparent λ_0^2 intermediate in value between its true λ_0^2 of $0\cdot07$ and its true λ^2 of $0\cdot03$. Similarly, borotartaric acid, with $\lambda_0^2 = 0\cdot024$, is apparently an example of Case III.*

(H +) against quantity of boric acid added will be discontinuous, following at first the equation :—

$$[H^+] = \sqrt{C_t}\, k_t + C_b\, (k_x - k_t).$$

and then the equation :—

$$[H^+] = \sqrt{C_b}\, k_b + C_t\, (k_x - k_t).$$

the break occurring when equimolecular proportions of boric and tartaric ac d are present in the solution. These equations are derived on the assumption that the combination occurs with the equilibrium completely on the borotartaric acid side. If the reaction is appreciably reversible, as appears probable from the fact that LOWRY and AUSTIN had to use $1\frac{1}{2}$ mols. of boric acid to one of tartaric in order to get " simple " dispersion, the equations are similar, but more complicated.

C_b and C_t represent the concentrations of boric and tartaric acids respectively present in solution, whether combined or not, and k_b, k_t and k_x represent the dissociation constants of boric, tartaric and borotartaric acids, respectively.

VII.

THE SPATIAL CONFIGURATION OF THE NORMAL CARBON CHAIN.

Much stress has been laid on the necessity for carrying out measurements of rotatory power with light of many different wave lengths and for studying the effect of dispersion. It cannot be denied, however, that a certain amount of progress has been made by means of work carried out with light of one wave length only. It is proposed to consider in the following paragraphs, one case in which our knowledge has been advanced by this means.

It is the custom, justified on the ground of convenience, to divide organic compounds into two great classes in order to facilitate the study of their behaviour. These classes are known as the " aliphatic " or straight-chain compounds, and the "aromatic " or ring compounds. Experience has shown, however, that the distinction between these types is one of degree rather than of kind, and we know, from the ease with which ring compounds—especially those with five or six atoms in the ring—can be formed from open chain compounds, that in many cases the actual closure of the ring is but a small operation— merely, as it were, the application of the match to the train that is already laid. In other words, the so-called " straight " carbon chain is not straight at all, but assumes a helical or spiral form in space, with five, or possibly six, atoms in one complete turn.

All this, of course, is far from new. It is in accordance with, though by no means a necessary corollary of, our conception of the tetrahedral disposition in space of the valency force directions of the carbon atom. But although the spiral form of the carbon chain is probable enough on chemical grounds, the effect of this configuration has hitherto been detected in no physical property except optical activity, and, to a very much less extent, molecular volume and refractive power. Its probable effect on optical activity was predicted as long ago as 1899 by FRANKLAND,[85] when he said that : " according to the commonly accepted views of stereo-chemistry, a continuous chain of five carbon atoms will all but return on itself, and beyond this, further additions to the chain will lead to such interference as must necessitate

a readjustment of the exact positions occupied by the carbon atoms in a shorter chain. It is surely highly probable that this stereo-chemical change should be betrayed by some irregularity in the rotatory manifestations, for example, by the exhibition of a maximum rotation in those series in which the ascent of the series leads to an increase in the rotatory power."

Broadly, then, we may say that it is not inconsistent with general chemical theory and experience to assume that the "open" carbon chain assumes a spiral form with about five atoms in one turn. It is at once obvious, however, that the spiral is not the only form which the carbon chain can assume, nor, considered from a purely statistical point of view, is it the most probable one. Consider, for example, the carbon atom to be a point with four equal valency forces directed from it to the four vertices of the regular tetrahedron of which it is the centre of gravity. Then, the angle between any two valency force directions—the "intervalent" angle—can be shown by elementary geometry to be $2 \tan^{-1} \sqrt{2}$ or $109.5°$, nearly. If, now, a chain of such atoms be constructed in such a way that the two valency force directions linking any two adjacent atoms lie in one straight line, it will be found that the first three members will lie in one plane. When, however, we proceed to add the fourth member, we have the choice of three points to which it may be attached, only one of which will lead to a helical configuration. That is to say that with a four membered chain, the probability of a spiral form being assumed as a result of pure chance is $1/3$. The same argument applies when we add the fifth and the succeeding members, and, in general, for an n membered chain, the probability of the formation of a spiral is $(1/3)^{n-3}$. As a fact, the actual probability will be much less than this, because, firstly, it can not be assumed in practice, as we have done above, that the carbon atoms are not free to rotate about the bond joining them, and secondly, the carbon atoms and their substituents possess a finite magnitude—they are not mathematical points, and it is therefore incorrect to assume that any three of them must lie in one plane. Both the tacit assumptions made in the above calculation, therefore, cause the probability deduced from it to assume a high value, and the actual value, though unknown, is certainly less than that given above.

The number of atoms in one complete turn of the spiral is easily calculated for the simple case considered. It is merely BAEYER'S Strain Theory over again. If the intervalent angle of the carbon atom were exactly 108°, one turn would contain just five atoms; if it were

exactly 120°, there would be exactly six atoms in one complete turn. As it is 109·5°, five atoms will nearly, but not quite, complete the turn. But the case is not nearly so simple as the rigid conceptions of VAN'T HOFF and von BAEYER would lead us to expect. The intervalent angle of the carbon atoms in a chain can never be 109·5°. If, as IN-GOLD has recently pointed out, the intervalent angle of the carbon atom depends on the space occupied by the various atoms or groups to which it is attached,[86] there are very few compounds known in which all the carbon atoms in the molecule can have valency force directions of equal mutual inclination,* and none of these can be optically active.

Then, again, we may have to consider the case of heterocatenic compounds. What will be the effect on the shape of the chain when an atom of an element other than carbon is introduced ? The answer is at present that we do not know, but that in some cases we are able to make a more or less intelligent guess. The oxygen atom, for instance, has a volume very nearly identical with that of the carbon atom, and, in addition, it is very frequently quadrivalent. It would seem not altogether unreasonable, therefore, to suppose, at all events as a first approximation, that an oxygen atom may replace a carbon atom in an aliphatic chain with little or no effect on the shape of the chain.

The Asymmetry of the Spiral.

The conception of the spiral form of the carbon chain brings a new form of molecular asymmetry to our notice, and, unless it be assumed that this particular form of asymmetry, like that of the crystals mentioned on p. 12, is not associated with optical activity, we are forced to recognise a new form of stereo-isomerism, and with it, of course, optical activity. This assumption is most improbable, since it has been shown that, for instance, quartz and crystals of tartaric acid owe their optical activity to a spiral arrangement of the molecules, and indeed, as it has been shown that optical activity can be produced artificially by building up what is practically a spiral structure of thin plates of mica. Thus, for example, stearic acid, with its normal chain of eighteen carbon atoms, should exist in two forms, a right-handed and a left-handed spiral. We might expect, then, to be able to resolve

---

* A little consideration will show that only compounds with one carbon atom in the molecule can fulfil this condition, and even then the carbon atom must be attached to four identical atoms or groups. We are thus confined to methane and the four carbon tetrahalides, with $C(NO_2)_4$, CN_4, CCr_4, and CFe_4 as very remote possibilities.

stearic acid into optical isomerides by, say, fractional crystallisation of its alkaloid salts from suitable solvents. Why has this never been done ? In the first place it has possibly never been attempted. As long as plane formulae for normal chain compounds are accepted, stearic acid appears to possess a symmetrical structure, and it would, therefore, appear a waste of time and effort to attempt to resolve it into enantiomorphs whose existence we have no reason to suspect. Preliminary experiments, however, have failed to show any resolution of this compound, and, although this can not be regarded as positive proof of the non-existence of enantiomorphous forms of stearic acid, we are left with the uncomfortable feeling that perhaps, after all, the hypothesis is in conflict with fact.

In order to clear up this point, let us investigate the connection between molecular asymmetry and optical activity rather more closely. Consider, first, space of two dimensions only. Suppose we have a race of intelligent beings whose whole existence and experience is confined to a plane : they can recognise length and breadth, but not thickness. Mathematicians amongst them would develop, no doubt, a system of geometry not very unlike that of EUCLID. But their limitations would produce differences between their plane geometry and ours. One of these differences is rather interesting from the point of view of optical activity.

EUCLID I, 8, states that if two triangles have three sides of the one equal to three sides of the other, each to each, then the triangles are equal in all respects. That is to say, that they are superposable. But the flat beings would distinguish two cases for all but isosceles triangles. Every scalene triangle would have one which is congruent with it and also one which is similar in all respects except that it is non-superposable upon the first by mere sliding in one plane. In the language of three dimensional space, the two triangles are related as are object and mirror-image, and, in order to effect superposition of one on the other, it is necessary to take one of them into space of three dimensions, turn it over, and replace it in its original plane.

In space of three dimensions there is an analogous case. Consideration of irregular tetrahedra of equal dimensions leads us to distinguish two cases precisely as did the flat beings. The tetrahedra may be superposable or they may not. In the latter case they are related as are object and mirror-image just as before. We may, therefore, suppose that if it were possible to take our irregular tetrahedron into space of four dimensions, and there perform upon it some operation

like turning it inside out, on returning it to space of three dimensions, it would fit on to its mirror-image.

The chemists amongst the flat beings would be similarly limited. To take one example, they would probably be able to detect isomerism in disubstituted derivatives of benzene when the substituents were different. They might, for instance, distinguish five isomeric cresols. 2-hydroxy toluene would be an enantiomorph of 6-hydroxy toluene ; 3-hydroxy toluene would similarly be enantiomorphous with 5-hydroxy toluene, but there would be only one form of 4-hydroxy toluene, or p-cresol. It is conceivable that they might be able to show some phenomenon allied to optical activity in these compounds.

It is interesting to note that we may obtain in three dimensional space a similar limiting effect by merely hydrogenating the three cresols. Ignoring geometrical (or *cis- trans-*) isomerism, we find that there exist two optically active hexahydroorthocresols, two optically active hexahydrometacresols, but only one hexahydroparacresol, and that is optically inactive.

Just as one of the flat beings might suggest that their kind of asymmetry and optical activity might disappear in space of three dimensions, it is now suggested that the kind of optical activity with which we are familiar might disappear if we could realise a space of four dimensions. In fact, short of actual decomposition, the only way in which an optically active compound of the VAN'T HOFF tetrahedral type can be converted directly into its enantiomorph is by removing it to four dimensional space, there performing a suitable operation upon it, and then replacing it in three dimensional space. The other way involves decomposition of the molecule, in that two of the groups attached to the asymmetric atom must be removed, transposed, and then replaced in their new, inverse order if it be desired to convert one optical isomer into the other.

But the case of the spiral is entirely different. Right and left-handed spirals are related as are object and mirror-image, but it is unnecessary to resort either to decomposition or to the fourth dimension to convert one into the other. All that is necessary for this conversion is a straightening of the spiral followed by a coiling up in the opposite sense. Therefore, if the spiral form of the carbon chain be regarded merely as one phase of a dynamic condition, rather than a permanently static one, we are brought to the conclusion that the spiral chain hypothesis does not lead necessarily to the postulation of a hitherto undetected form of optical activity.

It is not necessary, of course, that the coiling and uncoiling of the molecular chain should be rapid. In the liquid or dissolved state, a statistical equilibrium would be set up, which, if disturbed, would not require very rapid equilibration in order to avoid detection of the disturbance by the methods of resolution at present at our disposal.

The study of the natural rotatory powers of members of various homologous series has thrown a certain amount of light on this subject. It is found in general, that the magnitudes of the rotatory powers of the members of such series vary in a regular manner with molecular weight, and that, in addition, this regularity is often disturbed at perfectly definite points in the series, the normal variation being operative between such points. These points occur where an unbranched chain of carbon (or carbon and oxygen) atoms contains five, or a multiple of five, members, and we are thus enabled to extend FRANKLAND'S conception (p. 69) to some heterocatenic bodies containing one oxygen atom in the chain.

A few cases may now be considered. Irregularities are best detected by plotting rotatory powers as ordinates against molecular weight (or number of carbon atoms in the growing chain) as abscissae. A smooth curve is drawn, if possible, to connect the points, so that irregularities are betrayed at once. It is not strictly accurate, of course, to join the points by a smooth curve, because no meaning can be attached to points on it between the abscissae for integral numbers of carbon atoms, but if this limitation be borne in mind, the method is permissible.

Applying this method to the alcohols of the " methyl " series in the homogeneous state, we find an irregularity at methyl n-propyl carbinol,[87] where there is a chain of five carbon atoms, thus :—

$$\overset{1}{C}H_3 \cdot \overset{2}{C}H \cdot \overset{3}{C}H_2 \cdot \overset{4}{C}H_2 \cdot \overset{5}{C}H_3$$
$$\underset{OH}{}$$
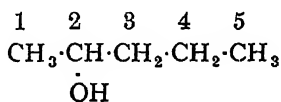
When these alcohols are examined in solution, irregularities are found in the rotatory powers of the n-propyl, n-amyl, n-octyl and n-decyl members.[88] These may obviously be divided into two pairs, the components of each pair differing in composition by five methylene groups, thus :—

$$\overset{1}{C}H_3 \cdot \overset{2}{C}H \cdot \overset{3}{C}H_2 \cdot \overset{4}{C}H_2 \cdot \overset{5}{C}H_3 \qquad \qquad \text{\textit{n}-propyl}$$
$$\underset{OH}{|}$$

$$\overset{1}{C}H_3 \cdot \overset{2}{C}H \cdot \overset{3}{C}H_2 \cdot \overset{4}{C}H_2 \cdot \overset{5}{C}H_2 \cdot \overset{6}{C}H_2 \cdot \overset{7}{C}H_2 \cdot \overset{8}{C}H_2 \cdot \overset{9}{C}H_2 \cdot \overset{10}{C}H_3 \qquad \text{\textit{n}-octyl}$$
$$\underset{OH}{|}$$

and

$$\begin{matrix} CH_3 \\ HO \end{matrix} \Big\rangle CH \!-\! \overset{1}{C}H_2 \cdot \overset{2}{C}H_2 \cdot \overset{3}{C}H_2 \cdot \overset{4}{C}H_2 \cdot \overset{5}{C}H_3 \qquad \text{\textit{n}-amyl}$$

$$\begin{matrix} CH_3 \\ HO \end{matrix} \Big\rangle CH \!-\! \overset{1}{C}H_2 \cdot \overset{2}{C}H_2 \cdot \overset{3}{C}H_2 \cdot \overset{4}{C}H_2 \cdot \overset{5}{C}H_2 \cdot \overset{6}{C}H_2 \cdot \overset{7}{C}H_2 \cdot \overset{8}{C}H_2 \cdot \overset{9}{C}H_2 \cdot \overset{10}{C}H_3$$
$$\text{\textit{n}-decyl}$$
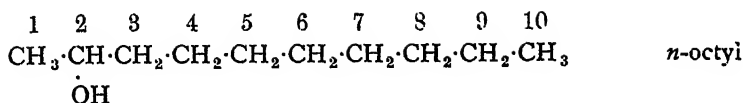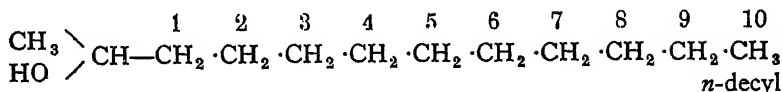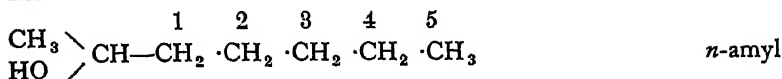
Thus, in the first case, the irregularities occur when the whole chain of carbon atoms in the molecule completes one or two turns of the spiral ; in the second case, the irregularities occur when the heaviest group attached to the asymmetric carbon atoms form a spiral chain completing a whole number of turns.

A similar case can be made out for the ethyl *n*-alkyl carbinols,[89] for the esters of *iso*pulegol,[90] and for the esters of methyl *n*-hexyl-,[91] ethyl *n*-hexyl-[92] and benzylmethyl carbinols.[93] There are isolated cases, too, which appear to support this hypothesis : these have recently been collected and the whole of the evidence reviewed and considered.[94]

It is fairly clear from the foregoing, that there is a good deal to be said in favour of a spiral configuration for the normal aliphatic chain on the evidence of optical activity alone. It has already been shown that such a configuration is not incompatible with our general knowledge of the reactions and properties of organic compounds. It is possible, too, that further light may be thrown on this problem by work carried out with the X-ray spectrometer by Sir W. H. BRAGG and his students on the crystal structure of aliphatic compounds. The work of ASTBURY on tartaric acid has already been referred to (p. 50), in which the optical activity of this compound is ascribed to a spiral configuration of the molecule. Here, however, we are confronted with a difficulty. In the theory advanced by the school under

PICKARD and KENYON, the spiral nature of the carbon chain is proposed, but some pains are taken to show that the spiral form assumed is not necessarily productive of optical activity. To do this, we are compelled to assume a dynamic condition of affairs, in that the carbon chain is supposed to be coiling up and uncoiling in a continual state of movement.

At this point, however, investigators working under BRAGG actually detect the spiral, but, instead of regarding it as a complicating factor in the problem, actually use this same spiral form to explain the optical activity of the solutions of the acid. This spiral configuration must therefore, even in solution, be essentially static in its nature. It is somewhat early yet, especially in the absence of further work on the crystal structure of aliphatic compounds, to attempt a reconciliation of the conflicting theories. But it may be that the conflict is more apparent than real. The dynamic form of the spiral may be the normal condition of the aliphatic chain—especially the hydrocarbon chain. In the molecule of tartaric acid, however, there are no less than six atoms of oxygen : four of these are undoubtedly exerting a higher valency than two. It does not, therefore, require a very great effort of the imagination to regard the molecule of tartaric acid as a spiral whose oscillations are cramped and nearly obliterated by the fact that the subsidiary valencies of the oxygen atoms are acting as ties and cross-ties, so that it is compelled to exhibit a rotatory power definite both in magnitude and in sign.

At first sight it is somewhat surprising that measurements of rotatory power, made with light of one wave length only, should lead to an advance of so fundamental a character as that considered in this chapter, in our knowledge of the configuration of the molecule. In view of these results, it might be wondered why the necessity for the study of dispersion should be emphasised. It is submitted that in this particular problem the effect of dispersion is automatically eliminated by the fact that the compounds studied form homologous series : that it is to be expected that the members of each series will exhibit a characteristic absorption band in the ultra-violet, and therefore all the members of the series will exhibit the same dispersive power. If this be so, then a comparison of the rotatory powers of the members for any standard wave length is equivalent to a comparison of the values of the more fundamental characteristic, the rotation constant. It is nearly certain, however, that no deductions of a quantitative nature can be made from the amount of exaltation or depression

of the rotatory power at the points of irregularity until much more work has been done and we are familiar with the effect of temperature and of solvents, not only upon the rotatory powers of such compounds, but also upon the magnitude of their rotation and dispersion constants

VIII.

Refractive Power.

The view adopted by the majority of the chemists of the present day appears to be that the property of refractive power is almost completely additive, in contrast with the highly constitutive nature of natural rotatory power. An attempt will be made, however, to show that refractive power is not as additive as is commonly supposed, but that an appearance of spurious additivity has been conferred upon it by the methods of calculation employed. No less than ten different formulae[96] for the computation of refractive power have been proposed from time to time, all of which, with the single exception of one due to EISENLOHR,[97] involve some function of the refractive index and the inverse of the density. Of these, probably the best known and least unsuccessful is that put forward simultaneously by LORENZ[98] of Copenhagen and LORENTZ[99] of Leiden :—

$$[R_L]_\lambda^t = \frac{(n_\lambda^t)^2 - 1}{(n_\lambda^t)^2 + 2} \cdot \frac{M}{d_4^t}$$

The only other formula to gain wide acceptance is that of GLADSTONE and DALE[100] :—

$$[R_G]_\lambda^t = (n_\lambda^t - 1) \cdot \frac{M}{d_4^t}$$

These formulae are empirical, although theoretical justification can be advanced for both of them. They are usually applied to the refractive index measured for the D line, and the values for the atomic refractive powers for the various elements are available for both formulae. These values have been determined in rather an arbitrary manner by the elimination of common groups from compounds of which the molecular refractive powers are known, and in no case do they represent the true specific refractive powers of the elements in the free state.

Originally it was intended to calculate atomic refractive powers for the various elements only, but as time went on and accurate experimental data accumulated, it was found that this was insufficient, and it became necessary to assign different values to the atomic refractive power of an element according to the method in which it was linked to other elements in a compound. Even this system broke down when unsaturated compounds were examined and values for the " atomic " refractive power of the double and triple bond were proposed.

Unfortunately, however, even this did not mark the end of the assumptions. It became necessary to modify the values of refractive power for compounds with conjugated systems of double bonds, conjugated systems of double bonds with ketonic groups, and even for conjugated systems of double bonds with halogens. It was found, too, that compounds with a ring structure did not fall into line with open chain bodies, and special effects were assigned to various types of ring structure.

It is apparent from the foregoing that the present methods of dealing with refractive power have required a good deal of bolstering up in order to achieve their results. It is submitted, however, that these results have very little theoretical significance : that they are, in fact, merely arithemetical consequences necessitated by the methods of calculation adopted.

The values for the atomic refractive powers of the elements do not agree amongst themselves. It will be apparent that

$$[R_L] \quad = \quad \frac{(n-1)(n+1)}{n^2+2} \quad \cdot \quad \frac{M}{d}$$

and that therefore

$$\frac{[R_L]}{[R_G]} = \frac{(n-1)(n+1)}{(n-1)(n^2+2)}$$

Now for the vast majority of organic compounds, n_D lies between 1·35 and 1·55, so that $[R_L] / [R_G]$ lies between $(1·35+1) / (1·35^2+2)$ and $(1·55+1) / (1·55^2+2)$, that is to say, between 0·61 and 0·58. It would appear reasonable, therefore, to expect that the atomic refractive powers of the elements for the " n " formula would all be greater than the atomic refractive powers for the same elements for the " n^2 " formula in the ratio 1 to 0·60. The following table shows that this is far from being the case.

| Element | Atomic Refractive Power | | Ratio of At. Refr. Powers |
	"n" formula ZECCHINI[101]	"n^2" formula EISENLOHR[102]	"n^2" formula /"n" formula
Carbon	4·71	2·418	0·514
Hydrogen ...	1·47	1·100	0·748
Oxygen (hydroxylic)	2·65	1·525	0·575
Oxygen (ethereal)	2·65	1·643	0·621
Oxygen (ketonic)	3·33	2·211	0·665
Chlorine ...	10·05	5·967	0·594
Bromine	15·34	8·865	0·578
Iodine	25·01	13·900	0·556
Double Bond ...	2·64	1·733	0·658
Methylene Group	7·65	4·618	0·604

Only three out of the nine values fall within the calculated limits and the greatest deviation amounts to nearly twenty-five per cent. It is obvious, however, that the values are such that for the majority of organic compounds either formula is suitable because the elements with a high "n^2/n" ratio are generally to be found linked to those with a low "n^2/n" ratio in such a way as to give a complex with the calculated ratio. This is well brought out by the value for the methylene group—the link from which the hydrocarbon chain is forged—which has the normal ratio, although the ratios for its constituent elements differ so widely from the calculated value.

The chief defect in the LORENZ and LORENTZ formula as at present used lies, however, in the fact that the values for the atomic refractivities of the elements are not expressed with sufficient accuracy, thus :—

$$R = \frac{n^2 - 1}{n^2 + 2}$$

$$\frac{dR}{dn} = \frac{6n}{(n^2 + 2)^2}$$

$$\text{or } dR = \frac{6n \cdot dn}{(n^2 + 2)^2}$$

$$\text{so that } \frac{dR}{R} = \frac{dn}{n} \cdot \frac{6n^2}{(n^2 + 2)} \cdot \frac{1}{(n^2 - 1)}$$

let $n = 1·414$ — a simple mean value —

$$\frac{dR}{R} = 3 \frac{dn}{n}$$

If, therefore, refractive indices are measured with an accuracy such that the figure in the fourth decimal place is significant (about the accuracy of a PULFRICH refractometer used with ordinary care), then, corresponding to this accuracy of one part in 15,000 in the refractive index, we require an accuracy of one part in 5,000 in the atomic refractive powers. That is to say, EISENLOHR'S values on p. 80 ought to be quoted, in six out of the ten cases, to one more place of decimals. But, as a fact, they are really much less accurate than they seem. They are all mean values from a large number of determinations, most of which vary considerably from the final mean. Let us consider the values for the methylene group and for hydrogen, these are certainly much more accurate than the rest. EISENLOHR quotes the following as the means of many independent determinations :—

Methylene group.

In hydrocarbons ...	...	...		4·6247
In polymethylenes	...	...		4·6324
In aldehydes and ketones		...		4·6265
In acids ...	...	...	...	4·6137
In alcohols	...	...	...	4·6343
In esters ...	...	...	...	4·6056
			Mean	4·6178

Hydrogen.

In paraffins	...	...	...	1·1352
In alcohols	...	...	...	1·0646
			Mean	1·0999

It will be seen that the variations are very considerable indeed, amounting to about 11 parts in 5,000 from the mean in the case of the methylene group in alcohols, and to about 160 parts in 5,000 from the mean in the case of both the values for hydrogen. It is small wonder, then, that refractivity continues to be regarded as an additive property when variations in the standard values corresponding to one hundred and sixty times the experimental error are tolerated. In practice, of course, these errors frequently act in opposite directions, but reliance on accidental compensations of this kind can hardly be dignified by the name of science. Two examples will, perhaps, make the matter clearer and also serve to indicate the order of magnitude of the error involved.

Hexane.

Let us suppose that hexane has just been synthesised for the first time. Its discoverer has to propose a formula for it, and after going through the usual routine of combustion, vapour density, reactions, and so on, decides on the formula and wishes to clinch the matter by a determination of the refractive power. When he comes to calculate the value of the molecular refractive power, he will, if he prides himself on keeping abreast of the times, use EISENLOHR'S published figures for atomic refractive power, and by so doing, he will get the value $6 \times CH_2 + 2 \times H = 27 \cdot 708 + 2 \cdot 200 = 29 \cdot 908$ and no doubt his observed figure will come very near this. But probably a more accurate value would be obtained by using the value for CH_2 in hydrocarbons and for hydrogen in paraffins, when we get $27 \cdot 7482 + 2 \cdot 2704 = 30 \cdot 0186$. The difference of 111 parts in 30,000 between these results represents a difference in the observed refractive index of 18 units in the fourth place.

n-*Undecyl Alcohol.*

In a similar case with this compound the following values would be obtained :—

From figures on p. 80. (the ones generally accepted).	Appropriate values from p. 81.
$11 \times CH_2 = 50 \cdot 798$	$50 \cdot 9773$
$2 \times H = 2 \cdot 200$	$2 \cdot 1292$
$1 \times O = 1 \cdot 525$	$1 \cdot 525$
hydrox. —·—	
$54 \cdot 523$	$54 \cdot 6315$

The difference between the values here represents a difference of 9 units in the fourth place in the refractive index. In this case, the deviations from the mean values of the atomic refractive powers are partially counterbalancing.

Examples could, of course, be multiplied *ad nauseam* : the plain fact of the matter is that EISENLOHR had no justification whatever for averaging the values quoted on p. 81—especially as he quotes the refractive indices from which they are calculated to five places of decimals. That is to say, he has ignored the first principles of scientific measurement by assuming that these values which differ from each other by many times—in one case hundreds of times—the possible

experimental error, are in reality identical, and are best represented by their mean.

It is very difficult, of course, to decide what differences are allowable in the individual values for atomic refractive power, but it is possible to say with some certainty what is the accuracy with which a refractive index or a density has been measured. The advocates of the view that refractive power is an additive property are therefore challenged to recalculate their figures so that, instead of quoting observed and calculated values for the refractive power, they work backwards from the calculated refractive power to obtain the calculated value for the refractive index which can then be compared with the observed value. This method will show at once whether the differences are within the limit of experimental error, a very desirable end, which is certainly not attained by the method of calculation at present in vogue.

Further, it must be considered that, in general, high refractive index and high density go hand in hand, so that their effects tend to counterbalance in the calculation of refractive power. It is then apparent that molecular refractive power becomes practically a function of molecular weight so that its additive nature is but a reflection of the additive character of molecular mass. This latter argument applies, though in less degree, to molecular refractive power calculated by means of the GLADSTONE and DALE formula.

It is not contended that this is a complete explanation of the additive nature of molecular refractive power, or even that this physical property has no additive characteristics. It is undoubtedly true that refractive power is to a certain extent additive in character, but it is submitted that the present methods of calculation tend to lay undue stress on this aspect, and do not bring out sufficiently the constitutive nature of the property. It is submitted, too, that the accepted values for the atomic refractive powers of the various elements which enter into the constitution of organic compounds are valueless. They achieve their results by a process of compromise and it is possible to obtain equally good results by using figures which differ from them by as much as ten per cent., provided that the adjustments are made in such a manner as to counterbalance one another when taken together in calculating the refractive power of an organic compound.

Something of this kind was probably in the mind of EISENLOHR when he suggested that molecular refractive power should be represented simply as the product of molecular weight and refractive index,

but although this proposal has greater theoretical justification than any of those which had been previously advanced, it has not yet been widely adopted, and possesses, in common with all its predecessors, the fundamental defect that it ignores completely the effect of dispersion.

EISENLOHR and WÖHLISCH suggest $M \times n_D^{20}$ as an expression for molecular refractive power and use the difference between calculated and observed values (the E—value) as a key to constitution. EISENLOHR[103] states that :—

" Der Vergleich dieses Wertes mit den aus Einzelkonstanten und Bildungs äquivalenten errechneten Grossen liefert uns das scharfe Instrument des E—Werts, der zum Einblick in den Molecülbau wie als Kriterium des Reinheitsgrades der Substanz ein unschatzbares Mittel darstellt."

But in view of the figures quoted by the author[104] this claim cannot be upheld.

IX.

Refractive Dispersion.

Refractive dispersion is a much more common phenomenon than rotatory dispersion for it is manifested whenever a beam of multichromatic light passes at other than normal incidence from one medium to another of different density. It is somewhat surprising, therefore, to find that so little attention has been devoted to the investigation of the connection between refractive dispersion and chemical constitution. It is true, of course, that measurements of refractive index for light of more than one wave length are sometimes made, and that the refractive dispersive power of a compound is occasionally measured as the difference between its refractive indices for two arbitrarily chosen lines of the spectrum (usually the C and G^l hydrogen lines). But the chemical significance of refractive dispersion has not yet been generally realised : one standard text-book on the subject of refractive power states that " it is clear that in order to obtain comparable values the refractive indices of substances must be measured with light of some standard wave length "[105]—a statement which shows that the author has utterly failed to realise the enormous importance of dispersion.

To show how thoroughly the effect of dispersion has been misunderstood, the following table shows CONRADY'S[106] figures for the values of the atomic refractive powers of various elements for the C and D lines of the solar spectrum for the formulae of GLADSTONE and DALE and of LORENZ and LORENTZ. These figures are the accepted standards from which all values of molecular refractive power were calculated during the twenty years between 1891 and 1910, and which even now are very frequently employed.

Element.	GLADSTONE and DALE.		LORENZ and LORENTZ.	
	R_c	R_D	r_c	r_D
Carbon singly bound, occurring alone	5·00	4·71	2·365	2·592
Carbon singly bound ...	—	—	—	2·501
Hydrogen	1·30	1·47	1·103	1·051
Hydroxyl oxygen	2·80	2·65	1·506	1·521
Ethereal oxygen			1·655	1·688
Ketonic oxygen	3·40	3·33	2·328	2·287
Ethenoid linkage	2·40	2·64	1·836	1·707
Acetylene linkage	—	—	2·27 or 2·48	2·10
Chlorine	9·79	10·05	6·014	5·998
Bromine	15·38	15·34	8·863	8·927
Iodine...	24·87	25·01	13·808	14·12

Now the wave length of the C hydrogen line is 6563 Å. U. and of the mean D line is 5893 Å. U., so that as we know that refractive index (and also, of course, refractive power) decreases with increasing wave length, it would appear reasonable to expect that the values of the atomic refractive powers for the D line would be uniformly higher than those for the C line. It will be seen that for the GLADSTONE and DALE formula, four values are higher for D than for C, and four are lower. For the LORENZ and LORENTZ formula, six values are higher for the D line than for the C line, whilst five are lower. Moreover, it is curious that, in general, these variations are in inverse order for the two formulae—if the atomic refractive power of an element for one formula is higher for the D line than for the C line, then for the other formula the reverse is the case. But the figures are not even consistent in their inconsistency as will readily be seen from a comparison of the values for ketonic oxygen for both formulae. These values have, however, been revised by EISENLOHR, whose new values take account of dispersion in that they lie on smooth curves when plotted against wave length. But it is not alone with compounds containing only carbon, hydrogen, and oxygen that difficulties arise with this method. No less than thirty-two values for the atomic refractive power of nitrogen have been collected by BRUHL,[107]

differing according to the method of combination of the element, and of these, three have values for the C line higher than the corresponding ones for the D line. For the other elements, there are not sufficient data available for a comparison to be made.

A little consideration will show at once that unless all organic compounds exhibit the same refractive dispersive power, any serious attempt to treat refractive power as an additive property is fore-doomed to failure if the refractive index for light of some arbitrarily chosen wave length as standard is used.

The phenomenon of refractive dispersion was first systematically studied by NEWTON,[108] who was the first to suggest a connection between refractive index (amount of deviation) and wave length. He came to the conclusion that for all substances, the dispersion was proportional to the refraction, that is that substances with high mean refractive indices have large dispersive powers and hence give wide spectra. This has since been shown to be erroneous, although it is true for many substances.

Anomalous Refractive Dispersion.

For the great majority of substances the refractive index increases with decreasing wave length. In 1885, CAUCHY[109] proposed a dispersion equation :—

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \cdots$$

This equation was extraordinarily successful, and has enjoyed a popularity which is only commencing to decline at the present time. The reasons for this popularity will become obvious when the SELLMEIER equation is discussed. It was found, however, that the CAUCHY equation was not always applicable to observations covering a spectral range extending beyond the visible region, and, in 1864, BRIOT[110] proposed a modified form of the equation, thus :—

$$\frac{1}{n^2} = k\lambda^2 + \frac{A}{\lambda^2} + \frac{B}{\lambda^4} + \cdots$$

These equations, however, whilst eminently satisfactory for the great majority of compounds, failed completely to account for anomalous refractive dispersion. This phenomenon, which is entirely distinct from the ordinary form of anomalous rotatory dispersion, was apparently first observed about 1840 by FOX TALBOT, who, however, paid very little attention to it, and later by LEROUX,[111] who observed it in the case of iodine vapour. Later still, it was observed and studied by CHRISTIANSEN,[112] who worked with solutions of fuchsine.

In all the cases of anomalous refractive dispersion, it was found that, in the case of coloured substances, the refractive index, instead of increasing steadily with decreasing wave length, as demanded by the equations of CAUCHY and BRIOT, increased rapidly near the less refrangible side of an absorption band, and assumed an abnormally low value on the more refrangible side. The refractive index actually decreased with decreasing wave length when crossing an absorption band. The phenomenon is thus completely analogous to the second type of anomalous rotatory dispersion mentioned on p. 27, although in the case of rotatory dispersion it has never been observed under conditions which are entirely free from objection. The following values were observed by COTTON for the rotatory power of chromium tartrate in the neighbourhood of its yellow absorption band :—

$$\lambda = \quad 657 \quad\quad 589 \quad\quad 581 \quad\quad 562 \quad\quad 522 \quad\quad 473 \text{ millimicrons}$$
$$\alpha = +1° 26' + 2° 30' + 1° 46' - 1° 21' - 2° 50' - 1° 52'$$

in which the effect on the rotatory power of crossing the band is very clearly marked (compare Fig. 5). Much more recently, LIFSCHITZ[113] has succeeded in observing a very similar effect with coloured metallic salts of hydroxymethylenecamphor. In neither of these cases, however, is the evidence entirely satisfactory. Solutions are employed in both examples, and in the case of the chromium tartrate there is the possibility of hydrolytic dissociation and the consequent presence in the solution of several optically active complexes. This objection has been met in the second case, where organic solvents are employed, but the active compounds possess molecules of great complexity, and, in addition, not all of the compounds examined, although they are apparently of the same chemical type, exhibit the phenomenon.

With anomalous refractive dispersion, however, the case is very different. It has been shown by WOOD to occur in a very striking manner at most of the absorption bands of the very complex spectrum of iodine vapour, and the same worker has also succeeded in demonstrating its occurrence in sodium vapour with its remarkably simple spectrum.

The discovery of anomalous refractive dispersion led to attempts to express this phenomenon in mathematical form. The first of these was made by MAXWELL,[114] who, in 1869, proposed a dispersion equation in the form of a question set at the University of Cambridge. What was substantially the same idea was published independently three years later by SELLMEIER. The equation, remarkable in its

formal similarity to that of DRUDE for rotatory dispersion, is generally known as the MAXWELL-SELLMEIER, or, shortly, as the SELL-MEIER equation, and assumes the form :—

$$n^2 = a^2 + \Sigma \ \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}$$

Each term of the summation contains two constants, just as in the DRUDE equation : b_0 may be regarded as the refraction parameter, and λ_0 as the dispersion parameter. In addition, there is the constant term a^2, which, when added to $\Sigma \ b_0$, represents the dielectric constant of the medium or the square of its refractive index for a stationary electric field. Each electronic free period has its corresponding term in this equation, and it is to be noted that the summation extends over every electronic vibrator in the molecule, and is not confined, as in the DRUDE equation, to those moving in asymmetric paths. It will readily be seen that the CAUCHY equation can be directly derived from the SELLMEIER equation when λ_0 is small compared with λ by expanding the denominator of the latter to a rapidly convergent series. As most of the chemical compounds which have been investigated with regard to their refractive properties are transparent in the visible and most of the easily accessible ultra-violet spectrum, it follows that λ_0 must be small in comparison with the wave lengths of light usually employed in the measurement of refractive index, so that the great success of the CAUCHY equation for these compounds is explained.

The SELLMEIER equation, however, suffers from the same defect as does the rotatory dispersion equation of DRUDE : it does not take into account the degradation of the light energy in the phenomenon of absorption ; consequently it may be expected to break down in the near neighbourhood of an absorption band when the influence of the neglected friction term begins to make itself felt. This defect was remedied by HELMHOLTZ[115] who in 1875, proposed another, but very similar equation, which was in turn modified by v. KETTELER in 1885.[116] The SELLMEIER equation, however, should express the facts with accuracy over the whole of the spectrum with the exception of the regions extending a few Å. U. on each side of the head of every absorption band, and as its application to experimental figures is much simpler than that of the later modifications, the increased theoretical accuracy obtained by the use of the latter by no means compensates for the extra labour involved.

It is proposed, then, to adopt the SELLMEIER equation as a rational basis for the expression of refractive dispersion. It is rather strange that it has not been done before, but except in very isolated instances, this equation has not been applied to chemical problems. What little really fundamental work has been done on the subject of refractive dispersion in relation to chemical constitution has been confined almost entirely to a determination of the constants of the CAUCHY equation for various substances. For instance, LORIA[117] has determined them for methane, ethane, ethylene, and acetylene, whilst BURTON[118] has done the same for argon and helium. CUTH-BERTSON and METCALFE[119] have applied the equation to helium, and to mercury, sulphur and phosphorus in the gaseous state. The cases of argon, helium, and mercury are particularly interesting, because, although they show bright line emission spectra in the visible region, yet their refractive dispersion can be expressed by the CAUCHY equation which takes no account of absorption. Now it is fairly well established that absorption spectra, at all events in the case of gases, are merely reversed emission spectra. It would thus appear, either that these gases under the conditions for which their refractive indices were determined are in a condition entirely different from that in which they emit bright line spectra—that is, that the position of an absorption band is determined by external conditions such as temperature and pressure, or that the refractometric observations in question were not carried out in regions of the spectrum sufficiently near to the absorption bands to allow their influence to be detected. The latter alternative is by far the more probable, since WOOD has shown for sodium vapour, and later, BEVAN[120] has shown for potassium vapour —both investigators using the method of crossed prisms which enables the dispersion curve actually to be seen and photographed—that anomalous dispersion actually does occur in the very near neighbour-hood of the characteristic lines in the spectra of these substances.

More recently, however, formulae of the SELLMEIER or HELM-HOLTZ-KETTELER type have been applied to a very few com-pounds. CUTHBERTSON and CUTHBERTSON[121] have applied the SELLMEIER equation to the refractive dispersion of the halogens, halogen acids, ozone, steam, the oxides of nitrogen, and ammonia. MARWIN[122] fitted the same equation to the refraction figures for carbon, silicon, tin, and titanium tetrachlorides, and antimony penta-chloride, whilst LÜBBEN[123] used the KETTELER formula to express the refractive dispersion of aqueous solutions of salts of the

alkali metals. These cases are, however, merely isolated ones ; up to the present no attempt has been made to apply a rational refractive dispersion formula to a series of organic compounds.

It is submitted, however, that the time is now ripe for such an attempt to be made. It has already been shown that the generally accepted formulae for the calculation of refractive power are much too crude for application to a delicate optical property like refractive index—it is this element of crudity which has ensured them their success up to the present. Moreover, the greater part of the material examined refractometrically in the past was transparent in the visible and near ultra-violet portions of the spectrum, and from the two facts in conjunction, it immediately becomes obvious that the earlier workers could afford with impunity to neglect the effects of dispersion. The light rays with which they worked had wave lengths so very far removed from those of the characteristic absorption bands of the substances they had to deal with that it was really a matter of indifference which line of the spectrum they chose as standard. The dispersion curves of their substances in the visible region of the spectrum were flat, and their absorption asymptotes were far away in the remote ultra-violet, so that very slight changes introduced by small changes in the position of the absorption asymptote from substance to substance were completely masked by the insensitive character of the formulae employed. With the refinement of experimental method, and, what is more important, with the ever-widening scope of the investigation to include substances of more complicated chemical structure, the accepted method has begun to break down. So long as the empiricist has to deal with simple organic compounds containing only carbon, hydrogen, and oxygen, his formulae serve him well enough—the absorption band controlling the dispersion is far removed from the region of observation. It now becomes clear why it is impossible to assign any one value to the atomic refractive power of elements of variable valency like nitrogen, sulphur, and phosphorus, why special values have to be introduced to account for the effect of double and triple bonds, why special values have to be assigned to the refractive effect of ring closure, and why still further modifications have to be introduced into the figures for conjugated systems of double bonds, or of ketonic groups, or of one with the other. All these effects tend to produce colour in the molecule, that is to say, that they bring the dominant absorption band in the spectrum of the substance nearer to the visible spectrum and thus cause the effects of dispersion to become more and

more marked. The inadequacy of the formulae for the calculation of refractive power is now no longer a sufficient cloak for concealing the neglect of dispersion and the method obviously breaks down. It is, therefore, suggested that a new method be adopted : that the form of the refractive dispersion curves for organic compounds be studied. If the constants of the dispersion equations are used for the purposes of comparison of one compound with another, the question of a standard wave length does not arise, and, provided that no attempt is made to obscure the issue by the use of formulae such as that of GLADSTONE and DALE or of LORENZ and LORENTZ, it may reasonably be hoped that the true nature of refractive power, showing in all probability strongly marked constitutive character, will be revealed.

X.

MAGNETIC ROTATORY POWER.

Since FARADAY'S discovery of the " magnetisation of light " very many investigations have been carried out with the object of measuring the amount of rotation imposed on a beam of polarised light traversing different media under the influence of a magnetic field. Solids, liquids, and gases were employed as media, and at first the accumulated data remained in a very chaotic state. It was found, however, that magnetic rotation occurs in the same absolute sense (depending only on the direction of the magnetic field) irrespective of the direction of the beam of light, thus being sharply differentiated from natural rotatory power. On account of this property, it becomes possible to magnify the rotation produced by a column of substance by reflecting the beam of polarised light back and forth through it, the only limit to this practice being imposed by the loss of intensity consequent on repeated reflections and absorption in the medium. In this manner, BECQUEREL, by causing a beam of polarised light to pass five times through a column of carbon bisulphide three metres long, was able to observe a rotation of 0·5° due to the earth's field alone. FARADAY discovered that the amount of rotation produced by a column of any medium is proportional to the difference of magnetic potential between the ends of the column, that is to say, proportional to the intensity of the magnetic field acting in the direction of the beam of light. As the physicist VERDET expressed his measurements of magnetic rotatory power in minutes of arc per centimetre length in a field of intensity one dyne per unit pole, it has become customary to call this figure the VERDET constant of a substance. On account of the difficulty of producing, maintaining, and measuring a uniform magnetic field, however, it soon became the practice to eliminate this difficulty by comparing the rotations of various media with that produced by a standard substance under the same conditions, subsequently reducing all the measurements to a comparable form from a knowledge of the VERDET constant of the standard. As a standard, BECQUEREL used carbon bisulphide, but this was soon abandoned

in favour of water, which was used by W. H. PERKIN, Senr., in all his investigations.

In 1882, PERKIN[124] introduced the density of the medium under examination into the denominator of the expression used for calculating magnetic rotatory power. He thus instituted the practice of comparing the rotations of equal masses of different substances rather than equal volumes, which before had been customary. By means of this device he was able to detect marked regularities in the magnetic rotatory powers of chemically similar compounds, and he became the pioneer investigator of the connection between magnetic rotatory power and chemical constitution.

PERKIN'S classical researches showed magnetic rotatory power to be additive in nature, with marked constitutive characteristics. He worked almost entirely with sodium light although he made a few desultory measurements with red lithium and green thallium light, and, as a result of many thousands of measurements, classified organic compounds into groups, the members of each group having rotatory powers expressed by the formula :—

$$M = S + 1 \cdot 023n$$

M being the molecular rotation, S a " series constant " characteristic of each group, and n the number of carbon atoms in the molecule. Expressed in another way, the magnetic rotatory power of the methylene group is equal to $1 \cdot 023$ for the D sodium line. This generalisation applies only to aliphatic compounds, and even then very rarely to the lower members of homologous series.

Generally speaking, magnetic rotatory power is considered to be a more constitutive property than refractive power, though it has not been so extensively studied. It is submitted that the similarity between the two properties is much closer than is generally supposed, at all events as far as their connection with chemical constitution is concerned. Physically, there is a close connection between the two, and, when refractive power is studied apart from the stultifying influence of the two formulae dealt with in Chapter VIII., it is highly probable that it will be found to be far more constitutive than is at present thought to be the case, and will resemble magnetic rotatory power very closely in its characteristics.

Attempts have been made to treat magnetic rotatory power as an additive property in much the same way as refractive power, but they have not succeeded to any great extent, and it cannot be said that this property is yet of any great use in elucidating chemical problems.

Magnetic rotatory dispersion is a phenomenon which has been practically untouched until recent years, having been neglected in the same extraordinary manner as the other properties we have considered. It is to be hoped, however, that its investigation will lead to considerable advances in our knowledge of the theory of magnetic rotation as a whole, and of its connection with chemical constitution in particular.

XI.

Magnetic Rotatory Dispersion and Wiedemann's Law.

Although the phenomenon of magnetic rotatory dispersion has been very little investigated, it has been known for a long time that the rotation varied approximately as the inverse square of the wave length. VERDET and BECQUEREL used the formula :—

$$\omega = \frac{kn^2 (n^2 - 1)}{\lambda^2}$$

where n is the refractive index of the medium for light of wave length λ, and this form was used also by the late LORD RAYLEIGH.[125] The expression was used not so much as a dispersion formula, pure and simple, but rather as an extrapolation formula for comparing results obtained for the same substance using light of different wave lengths. In 1851, it was discovered by WIEDEMANN[126] that, in the case of turpentine, the magnetic rotatory power was proportional to the magnetic rotatory power over a range of five wave lengths in the visible spectrum, and accordingly he formulated the law bearing his name of proportionality of natural and magnetic rotatory powers. Subsequent investigators[127] sought to verify or to discredit this law, and sometimes drew diametrically opposed conclusions from very similar evidence. In 1912, LOWRY[128] published the results of a series of very accurate measurements of the natural and magnetic rotatory dispersions of quartz in the visible spectrum and showed that WIEDEMANN'S law held good for this body. In 1914, LOWRY, PICKARD, and KENYON[129] published a comparison of the natural and magnetic rotatory dispersions of a number of organic liquids and concluded that WIEDEMANN'S law did not hold good for these substances. Before examining these results and conclusions more closely, however, one might with advantage consider the various dispersion equations which have been proposed from time to time on theoretical grounds.

From electronic considerations, DRUDE[130] has proposed two equations for magnetic rotatory dispersion :—

(a) on the hypothesis that the magnetic field produces molecular currents within the medium :

$$\omega = n \left\{ \frac{a}{\lambda^2} + \Sigma \, \frac{b_0}{\lambda^2 - \lambda_0^2} \right\} \quad \ldots \ldots \quad (1)$$

(b) from a consideration of the HALL effect :

$$\omega = \frac{1}{n} \left\{ \frac{A}{\lambda^2} + \Sigma \, \frac{B_0 \lambda^2}{(\lambda^2 - \lambda_0^2)^2} \right\} \quad \ldots \ldots \quad (2)$$

BECQUEREL has proposed a third equation :—

$$\omega = k \lambda \, \frac{dn}{d\lambda} \quad \ldots \ldots \ldots \ldots \quad (3)$$

but as it does not appear to have at present any obvious bearing on chemical problems, and indeed does not fit the observed facts as well as the other two, it will not be further considered here.

Anomalous Magnetic Rotatory Dispersion. It is an experimental fact that very few substances exhibit negative magnetic rotatory power, and it may be said that all organic compounds exhibit positive magnetic rotatory power. It therefore follows that no organic compound will exhibit that kind of anomalous magnetic rotatory dispersion, the analogue of which is so common amongst organic compounds exhibiting natural rotatory power. Therefore, the only type of anomalous magnetic rotatory dispersion which is to be looked for amongst organic compounds is that which is associated with the presence of an absorption band in the region of experimental observation. Here we have a means of distinguishing between the dispersion equations (1) and (2). It will be observed that in equation (1), as λ, in decreasing, passes through the value λ_0, the terms after the first assume the value $\pm$ infinity, and become negative on the short wave length side of the band. In equation (2), however, the denominators of the terms after the first are the squares of the quantities $(\lambda^2 - \lambda_0^2)$, etc., and so the terms do not change sign in crossing the bands. There is thus a fundamental difference in the character of the dispersion curves demanded by equations (1) and (2) in the neighbourhood of the dominant absorption bands. Equation (1) demands a change in the sign of the rotation on crossing a band : equation (2) does not. An experimental test of this condition is not easily realised, but WOOD[181] has succeeded in showing that for an aqueous solution of a didymium salt, the magnetic rotation does not change sign on crossing its yellow absorption band. MACALUSO and CORBINO[132] have shown the effect for sodium vapour in the neighbourhood of the D lines, whilst WOOD[133]

has actually succeeded in fitting a one term equation of type (2) to the magnetic rotatory dispersion of sodium vapour in the same region. The rapid upward sweep of both limbs of the dispersion curve in the neighbourhood of the asymptote at 5893 Å.U. is a most striking feature in his results. It is, of course, not justifiable to assume on this evidence that equation (2) is the correct one to apply to organic compounds, but, in the absence of other evidence, it certainly points in that direction.

LOWRY[134] and his collaborators have adopted for magnetic rotatory dispersion an equation of the DRUDE type for natural rotatory dispersion :—

$$\omega = \frac{c_0}{\lambda^2 - \lambda_0^2} \qquad \cdots \qquad \cdots \qquad (4)$$

and they assert that all the compounds they have so far examined require only one term in such an equation to express their magnetic rotatory dispersion. Their choice, however, would seem to be unfortunate for several reasons :—

(a) It is quite conceivable that a substance should exhibit simple natural rotatory dispersion but complex magnetic rotatory dispersion. The converse case, however, seems much less likely. Natural rotatory dispersion is affected only by those electrons within the molecule which move in asymmetric paths : refractive dispersion, on the other hand, is affected by all the vibrating electrons in the molecule (provided, of course, that their periods are sufficiently small) whether they move in asymmetric paths or not. It would seem legitimate, too, to assume that the phenomenon of magnetic rotatory dispersion is due to the fact that the magnetic field imposes an element of asymmetry on the paths of all the electrons controlling refractive dispersion. The process may perhaps be regarded as follows. In the absence of a magnetic field, the electrons causing refractive dispersion are moving in circular orbits which are, of course, symmetrical. The component of the magnetic field perpendicular to the planes of the orbits of these electrons would cause them to move in helical paths and hence cause rotation of the plane of polarisation. Unless, therefore, it is assumed that the magnetic field acts selectively and influences certain electrons rather than others, which seems at present an unnecessary multiplication of hypotheses, it would appear

impossible for fewer electrons to influence magnetic than natural rotatory power.

(b) Again, if we consider a substance which exhibits both simple magnetic and simple natural rotatory dispersion, we see that its magnetic and natural rotatory dispersion ratios for any two wave lengths must be identical unless it is assumed that a magnetic field alters the position of the dominant absorption band. In other words, these investigators make two incompatible statements in their paper on the comparison of the magnetic and natural rotatory dispersions of organic liquids :—

(i.) that the equation $\omega = c_0/(\lambda^2 - \lambda_0^2)$ can be applied to the magnetic rotatory powers of many organic liquids ;

(ii.) that WIEDEMANN'S law is not valid for these liquids.
One of these statements may be correct ; both of them cannot be.

(c) It may be argued, of course, that the effect of the magnetic field is to cause a shift in the position of the dominant absorption band in the spectrum of the substance so that the two incompatible statements in (b) may be reconciled. Were this the case, then we should expect the shift to be proportional to the strength of the field, so that the dispersion would vary with the field strength and it would be futile to propose a dispersion equation which does not take account of this fact. The only other way out of the difficulty appears to be to assume that the effect of the magnetic field is to suppress one band entirely and to bring another into prominence—an hypothesis which is very difficult to accept.

*The Natural and Magnetic Rotatory Dispersions of Ethyl Tartrate.**

The considerations discussed above are well illustrated by the optical properties of ethyl tartrate. It is well known that the natural rotatory dispersion of this compound can not be expressed by a DRUDE equation with one term. LOWRY and CUTTER[135] have recently shown that its rotatory power can be expressed—at least in the visible and near ultra-violet regions of the spectrum—by the equation :—

$$[a] = \frac{25\cdot005}{\lambda^2 - 0\cdot03} - \frac{20\cdot678}{\lambda^2 - 0\cdot056}$$

*See Appendix.
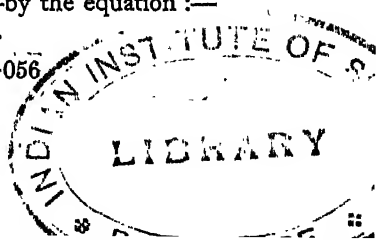
which predicts the presence of absorption bands at $\lambda \sqrt{0 \cdot 03}$ and $\sqrt{0 \cdot 056}$, that is, at λ 1730 and 2370 Å.U. LOWRY, PICKARD, and KENYON recognise the fact that ethyl tartrate exhibits complex natural rotatory dispersion, yet they say that its magnetic rotatory dispersion can be expressed by an equation of type (4), containing only one term. They do not give this equation, but they quote its dispersion ratio: $\omega_{4358}/\omega_{5461} = 1 \cdot 630$.

From this we have :—

$$\frac{\cdot 5461^2 - \lambda_0^2}{\cdot 4358^2 - \lambda_0^2} = 1 \cdot 680$$

whence $\lambda_0^2 = 0 \cdot 0179$, or $\lambda_0 = 1350$ Å.U.

The differences between this value and both of those obtained by LOWRY and CUTTER are far too great to be ascribed to experimental error. It is inconceivable, too, that the position of the dominant absorption band can have been moved at least 400 Å.U. merely by the application of a magnetic field as assumed by LOWRY, PICKARD, and KENYON. It seems far more probable that the magnetic rotatory dispersion of ethyl tartrate is represented by the equation :—

$$\omega = \frac{A}{\lambda^2} + \frac{B}{\lambda^2 - 0 \cdot 03} + \frac{C}{\lambda^2 - 0 \cdot 056}$$

in which A is very large compared with B or C. Then, with measurements confined to the visible spectrum, the form of the equation would appear to be :—

$$\omega = \frac{D}{\lambda^2 - \lambda_0^2}, \text{ where } \lambda_0^2 \text{ is less than } 0 \cdot 03.$$

The adoption of the dispersion equation :—

$$\omega = \frac{A}{\lambda^2} + \Sigma \frac{B}{\lambda^2 - \lambda_0^2}$$

would also explain the fact that, in general, magnetic rotatory dispersion ratios are less than the corresponding natural rotatory dispersion ratios. Where the converse is the case, it is probable that the substance in question possesses a refractive absorption band of greater wave length than its rotatory absorption band.

It is submitted, therefore, that there is no such phenomenon as simple magnetic rotatory dispersion in the same sense as simple natural rotatory dispersion : that the general form of magnetic rotatory dispersion equation may be taken to be :—

$$\omega = \frac{A}{\lambda^2} + \Sigma \frac{B_0}{\lambda^2 - \lambda_0^2} \qquad \cdots \cdots \cdots \quad (5)$$

but that, because of the fact that the individual terms are all positive and that some of them may be very small, an average term can, and often does, replace the actual ones with little loss of accuracy as far as measurements in the visible region of the spectrum, remote from the absorption bands, are concerned.

Quite recently, measurements of the magnetic rotatory dispersion of some organic compounds have been made in the near infra red spectrum by INGERSOLL.[136] This investigator is inclined to prefer the formula $\omega = k\lambda.dn/d\lambda$ to express his results, but an inspection of his curves shows clearly that this formula is not the one best fitted for his purpose. The deviations which he ascribes to experimental error are nearly all in one direction, and appear to point definitely to equation (5) as being more suitable.

STEWART[137] has suggested that interesting results might be obtained by placing optically active substances in a magnetic field of such a strength that the natural rotation is just counterbalanced by the magnetic rotation, thus giving a measure of optical rotatory power in absolute units. From what has already been said with regard to the inequality of natural and magnetic rotatory dispersions, it follows immediately that such a neutralisation could be obtained only for one wave length at a time, so that useful results are not to be expected from this method at least until we know much more about the phenomena of optical dispersion.

XII.

Dispersion and Absorption.

We are now in a position to compare the three dispersion equations. As the equations themselves are of such recent application, it can hardly be expected that much that is definite should be known about their constants. For convenience, it will be desirable to divide them into two classes :—

(1)   The numerator constants :
k_0, etc., for natural rotatory dispersion.
a^2, b_0, etc., for refractive dispersion, and
A, B_0, etc., for magnetic rotatory dispersion.

(2)   The denominator constants :
λ_0, etc., in all three equations.

With regard to class (1), practically nothing can be said. These constants are affected by temperature and probably by solvents, and our next experimental advance must be the investigation of the form of the function connecting them with temperature and possibly with pressure.   In a very interesting paper, HAVELOCK[138] discusses this problem for refractive dispersion as far as the scanty experimental figures at his disposal will allow him, and comes to the conclusion that the effect of the physical condition of the medium on dispersion is represented by two quantities—the density, and another quantity which represents the effect of the surrounding molecules.

Class (2) is the more interesting one at present : the first question that arises will be : Is λ_0 the same in all three equations ? It would be premature to give a definite answer at present, but an affirmative one seems highly probable with the provision that all rotatory electrons influence the refraction, but that all the refractive electrons do not necessarily influence the natural rotation, just as every admiral is a sailor, bur every sailor is not an admiral. It is highly probable, too, that all refractive electrons influence the magnetic rotation.

The second question will be : Is λ_0 the wave length of a real absorption band or merely a theoretical chimera ?   There is very little evidence on the point. The work of WOOD on sodium vapour, and of BEVAN on potassium vapour seems conclusive evidence of the

real existence of the band as far as metallic vapours are concerned. In the case of quartz, LOWRY proposes the equation :—

$$a = \frac{11 \cdot 6064}{\lambda^2 - 0 \cdot 010627} + \frac{13 \cdot 42}{\lambda^2 - 78 \cdot 22} - \frac{4 \cdot 3685}{\lambda^2}.$$

degrees per millimetre, for its rotatory dispersion in the visible spectrum from $\lambda 6708$ to $\lambda 4858$, and obtains agreement between the observed and calculated figures of about one part in 25,000. The writer has applied GIFFORD'S[139] figures for the refractive index of quartz to the determination of a SELLMEIER equation, using the same values for the wave lengths of the absorption bands and finds, for the ordinary ray :—

$$n^2 = 1 \cdot 35375 + \frac{1 \cdot 00317\, \lambda^2}{\lambda^2 - 0 \cdot 010627} + \frac{0 \cdot 8275\, \lambda^2}{\lambda^2 - 78 \cdot 22}$$

This gives an agreement between the observed and calculated figures of about one part in 150,000 over a range of the spectrum from $\lambda 7950$ to $\lambda 3303$. As quartz is known to exhibit absorption bands at about 1000 A.U. and 9μ, it would appear not only that the values for λ_0, etc., are the same for refractive as for rotatory dispersion, but also that these bands actually do exist.

In the case of organic compounds, however, the problem is much more difficult. The majority of them are so transparent in the region of the spectrum at present accessible to experimental observation that absorption is difficult to detect, so that anything like a systematic and extensive direct test of the validity of these equations is almost impossible. The whole question therefore resolves itself into one of obtaining a coloured optically active compound, so that, at all events, λ_0 may be determined from its natural rotatory dispersion and from its refractive dispersion, and then by direct measurement. It is advisable that this compound should be liquid, in order to eliminate the necessity for solvents. Such a compound is found in d-γ-nonyl nitrite,[140] from which, although the experimental conditions were rather difficult, it was found possible to derive the equations :—

$$a = \frac{0 \cdot 76}{\lambda^2 - 0 \cdot 135} + \frac{0 \cdot 43}{\lambda^2}$$

and

$$n^2 = 2 \cdot 0266 + \frac{0 \cdot 00127}{\lambda^2 - 0 \cdot 14} - 0 \cdot 0626\, \lambda^2$$

whence $\lambda_0 = 3680$ A.U., from measurements of rotatory power,

$\lambda_0 = 3730$ A.U., from measurements of refractive index,

and $\lambda_0 = 3670 - 3720$ by direct photographic measurement.

It is not wise, perhaps, to generalise too broadly on such meagre evidence, but it would certainly appear not unreasonable to hope that these dispersion equations will apply generally to organic compounds, and that the absorption bands which they predict will prove to have a very real existence.

We come now to the effect of external conditions on λ_0. The fact that the natural rotatory dispersion ratios of compounds exhibiting simple rotatory dispersion remain constant over temperature ranges of 180° C[141]., makes it very improbable indeed that change of temperature has any effect on the value of λ_0. Solution, however, is likely to have a very profound effect. KUNDT[142] has shown that the absorption bands of a solute are generally moved towards the less refrangible end of the spectrum with increase in the refractive index of the solvent. v. KAZAY[143] has verified this, and shown that it should be possible to calculate the amount of shift from a knowledge of the refractive indices of solute and solvent. The shift is regarded as a DOPPLER effect, and the equation proposed has the form :—

$$\lambda_1 + \lambda_0 \left(1 \pm c/v\right)$$

where λ_1 is the wave length of the shifted band,
λ_0 is the wave length of the original band,
c is the difference of the velocities of light in the solute and in the solution, and
v is the velocity of light in air.

This equation certainly appears to have possibilities when we come to consider the effect of solution on dispersion.

It is now becoming increasingly clear that measurements can no longer be carried out with substances in the homogeneous state only. For the measurement of absorption especially, it will be necessary to employ solvents. It is, therefore, imperative to study the effect of solvents on the optical properties of organic compounds. The proposed method of attack has not previously been employed, as far as is known, by any investigator in this field. It is proposed to study the effect of solvents from the point of view of their effect on the dispersion, both rotatory and refractive, of organic compounds. The first step is to investigate the effect of solution in all concentrations on the dispersion of a compound which exhibits simple rotatory dispersion. For the preliminary investigation,[144] d-β-octanol has been chosen as the optically active substance, and benzene and pyridine as the solvents.[144] For the purpose of comparison, a closely related compound, d-β-octyl

acetate, which exhibits complex rotatory dispersion under some experimental conditions, is being examined in the same two solvents. From the results, it would appear that, in the case of β-octanol, at all events, solution apparently does not introduce a second term into the DRUDE equation, that is to say, that with this compound as solute, and benzene or pyridine as solvents, solvation occurs, if at all, to a very slight degree. One result of interest, however, has already emerged from this investigation. It is found that the dispersion ratio $\alpha_{4358}/\alpha_{5461}$ of β-octanol undergoes a slight, but definite and progressive change with concentration. This can have only one interpretation : solution causes a change in the position of λ_0, the dominant absorption band in the spectrum of the compound. This result is not altogether unexpected ; in fact, it was because it was expected that the use of solvents was excluded from these investigations for so long. But it is not known upon what factors it depends. For the present, a working hypothesis is adopted that this shift in the position of the band is due to the DOPPLER effect mentioned above and is connected in some way with the refractive properties of both solute and solvent. If this result can be substantiated, and especially if the truth of the working hypothesis can be established, several important theoretical results will follow immediately.

Firstly, it will become clear why refractive power does not obey the mixture law, especially when the components of the mixture have refractive indices which differ widely. Secondly, some light may be thrown on the exceedingly complex problem of the effect of solvents on optical rotatory power. Thirdly, it will probably become necessary completely to revise most of our ideas on absorption spectra. Nearly all absorption measurements have been made in solution—ethyl alcohol has been very generally employed, because it is remarkably transparent in the ultra-violet region of the spectrum—and the tacit assumption has been made that the mixture law holds for the absorption of light. Evidence is accumulating, however, which shows that this is by no means the case, and it may be found that not only is absorption not an additive property in this sense, but also that it is highly constitutive in that the position of the bands in the spectrum depends on the chemical nature of both solute and solvent.

Fortunately, the investigations now being carried out offer us a means of studying this problem. If two substances can be obtained which are liquid, which can be obtained in both optically active and inactive forms, which are infinitely miscible, and of which one shows

selective absorption in or near the visible spectrum, it should be possible to attack the problem in the following manner. First, the inactive form of one substance is used as a solvent for the active form of the other and any change in the position of the dominant absorption band of the latter due to solution in the former is studied polarimetrically and, if possible, directly. The position is then reversed, solvent and solute change places with regard to their optically active states, and the effect of one on the dominant absorption band of the other is studied, again, if possible, both polarimetrically and directly. From the results obtained, it should then be possible to predict accurately the rotatory and dispersive power of any mixture of the two active compounds, and the validity of the hypothesis will stand or fall by the measure of success attained in this last operation. It is quite possible that we shall be unable to interpret the results of the measurements with β-octanol and benzene and pyridine until the results of experiments with mixtures of two optically active liquids are available. It is therefore considered advisable to commence work on this last problem with the least possible delay, and accordingly camphyl carbinol and β-octanol have been selected as the first pair. Camphyl carbinol is easily prepared, is liquid at ordinary temperatures, has a high rotatory power, and, further, exhibits apparently simple rotatory dispersion in the visible spectrum at least, with $\lambda_0 = 3200$ Å.U. A second pair, tetrahydrofurfurylcamphor and β-octanol, has been provisionally selected, provided that the former compound, which is known to be liquid and to possess a high rotatory power, shows apparently simple rotatory dispersion and has a suitable value for λ_0.

XIII.

Conclusion.

As a result of the considerations detailed in the preceding pages, it is proposed :—

(1) That the study of the phenomena of optical dispersion in organic compounds should be pursued with energy as being likely to yield results of theoretical value.

(2) That, for this purpose, the DRUDE equation, which has already been successfully applied fairly extensively in this field, is eminently suitable as a rotatory dispersion equation :

$$a = \Sigma \; \frac{k_0}{\lambda^2 - \lambda_0^2}$$

(3) That the SELLMEIER equation, which has been successfully applied, although in only a few cases, is eminently suitable as a refractive dispersion equation :

$$n^2 = a^2 + \Sigma \; \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}$$

(4) That a modified form of the DRUDE equation, which, however, has not yet been applied to experimental figures, is suitable for a magnetic rotatory dispersion equation :

$$\omega = \frac{A}{\lambda^2} + \Sigma \; \frac{B_0}{\lambda^2 - \lambda_0^2}$$

(5) That the dispersion constant in all these equations, represents, in general, the square of the wave length of the dominant absorption band in the spectrum of the substance under consideration, and that this band can, under suitable conditions, be shown to have a real existence. Each term in a dispersion equation represents the effect of one such absorption band on the physical property under investigation.

When we consider the four optical properties, natural and magnetic rotatory power, refractive index and absorption of light, we are immediately struck by the fact that, whilst the first of these properties is almost entirely constitutive in its nature, the other three possess decided

additive characteristics. A possible explanation of this is afforded by the consideration of the electron as the basic cause of chemical and physical behaviour. Workers in the domain of sub-atomic chemistry and physics have shown that the chemical and physical properties of the atom are very largely determined by the electrons in its outer shell. It would appear legitimate to extend this conception to the molecule, and to consider its properties as largely electronic in origin. In the case of organic compounds we are led to the conclusion that the electrons associated with atoms of carbon and hydrogen are subordinated to those associated with the atoms of other elements in the molecule. In this way we are provided, not only with an explanation of the similarity in properties, both chemical and physical, within homologous series, but also given an insight into the cause of the difference in behaviour between series of different chemical function.

Owing to the connection between asymmetry and natural rotatory power, it must nearly always happen that the characteristic group of an optically active molecule is attached to the asymmetric carbon atom and thus it would appear not unreasonable to assume that it is the electrons of this group which dominate the natural rotatory power of organic compounds, thus conferring upon this property a highly constitutive character. To the fact that the activities of the other electrons are not entirely suppressed must be ascribed the few additive relationships which have been detected.

With the remaining optical properties, on the other hand, there is no necessity for asymmetry of form, so that the characteristic group may assume any position in the molecule and can not dominate the situation to nearly the same extent. These properties are therefore constitutive, but with highly additive characteristics.

We are then brought to the conclusion that the electron is the unit which controls the natural and magnetic rotatory dispersion and the refractive dispersion of organic compounds, determines the positions of the bands in their absorption spectra, and determines broadly their chemical behaviour : it is to the behaviour of the electron that we must look for a further explanation of these physical and chemical properties of the molecule.

It must not be assumed, however, that the problem is simple. Even in the study of optical properties it is far less simple than even our most complex theories would lead us to expect. The vibrations within the molecule are not always electronic in size and character. It is generally understood that for radiations of shorter wave length than

about 2 or 3 μ, the vibrations are mainly electronic, but that, whilst there is no abrupt transition, for radiations of greater wave length than this, atomic and molecular vibrators are called into play.

It must be clearly understood, too, that in all these simple dispersion formulae, the actual absorbing system of the molecule is replaced by an ideal one, consisting of one or two electrons vibrating at definite frequencies. The agreement of prediction with experiment will, therefore, depend upon several conditions. The vibrating system may actually be so simple that it corresponds with the ideal case, when very good agreement is to be expected. Alternatively, it may consist of several more or less equal systems, when the value deduced from dispersion measurements will be a mean of the actual ones. A third case would exist when there are several systems, some of which are more predominant than others—the predicted value will then be a weighted mean of the actual ones and we should expect to obtain very different results by varying the experimental limits of the observations according as measurements are carried out in the vicinity of one or other of the bands. This last case is undoubtedly the most interesting, as it will possibly prove to be also the most common, of all conceivable cases.

XIV.

APPENDIX.

The Natural and Magnetic Rotatory Dispersions of Ethyl Tartrate.

The magnetic rotatory power of ethyl tartrate is not quoted in the literature, but by making $\omega = 1\cdot000$ for $\lambda = 5461$, we get the following equation, if

$$\frac{\omega_{4358}}{\omega_{5461}} = 1\cdot630$$

$$\omega_1 = \frac{0\cdot28}{\lambda^2 - 0\cdot018} \quad \cdots \quad \cdots \quad (1)$$

whence ω for all values of λ may be calculated.

If we now put

$$\omega_2 = \frac{k_1}{\lambda^2 - 0\cdot03} + \frac{k_2}{\lambda^2 - 0\cdot065} \quad \cdots \quad (2)$$

and make ω calculated from equation (2) equal to that calculated from equation (1) at $\lambda = 4000$ and $\lambda = 6000$ Å.U., we get

$$\omega_2 = \frac{0\cdot367}{\lambda^2 - 0\cdot03} - \frac{0\cdot0894}{\lambda^2 - 0\cdot056}$$

Again, by writing

$$\omega_3 = \frac{a}{\lambda^2} + \frac{b}{\lambda^2 - 0\cdot03} + \frac{c}{\lambda^2 - 0\cdot056} \quad \cdots \quad (3)$$

and making ω equal to the values calculated from equations (1) and (2) at $\lambda = 4000$, 5000 and 6000 Å.U., we get

$$\omega_3 = \frac{0\cdot078}{\lambda^2} + \frac{0\cdot239}{\lambda^2 - 0\cdot03} - \frac{0\cdot037}{\lambda^2 - 0.056}$$

whence

λ	ω_1	ω_2	ω_3	
2500	6·33	—10·88	—0·53	
2520	6·23	—1·66	+3·20	
2550	5·96	+0·56	3·91	
2600	5·60	2·22	4·35	
2700	5·08	3·28	4·44	
2800	4·67	3·58	4·30	
2900	4·25	3·61	4·04	
3000	3·89	3·50	3·76	
3500	2·69	2·64	2·68	
4000	1·97	1·97	1·97	
4358	1·63	1·63	1·63	
4500	1·52	1·52	1·52	
5000	1·21	1·21	1·21	Identical
5461	1·00	1·00	1·00	throughout
5500	0·98	0·98	0·98	the visible
6000	0·82	0·82	0·82	spectrum.
6500	0·69	0·69	0·69	
7000	0·59	0·59	0·59	

It is obvious, therefore, that there is no justification for the statement that ethyl tartrate shows simple magnetic rotatory dispersion (*see* Fig. 20).

FIG. 20.

A: $\varepsilon = 0.28/(\lambda^2 - 0.018)$

B: $\varepsilon = 0.078/\lambda^2 + 0.239/(\lambda^2 - 0.03) - 0.037/(\lambda^2 - 0.056)$

C: $\varepsilon = 0.367/(\lambda^2 - 0.03) - 0.089/(\lambda^2 - 0.056)$

$\lambda^2 = 0.018$: asymptote to A

$\left.\begin{array}{c} \lambda^2 = 0.03 \\ \lambda^2 = 0.056 \end{array}\right\}$ asymptotes to B and C
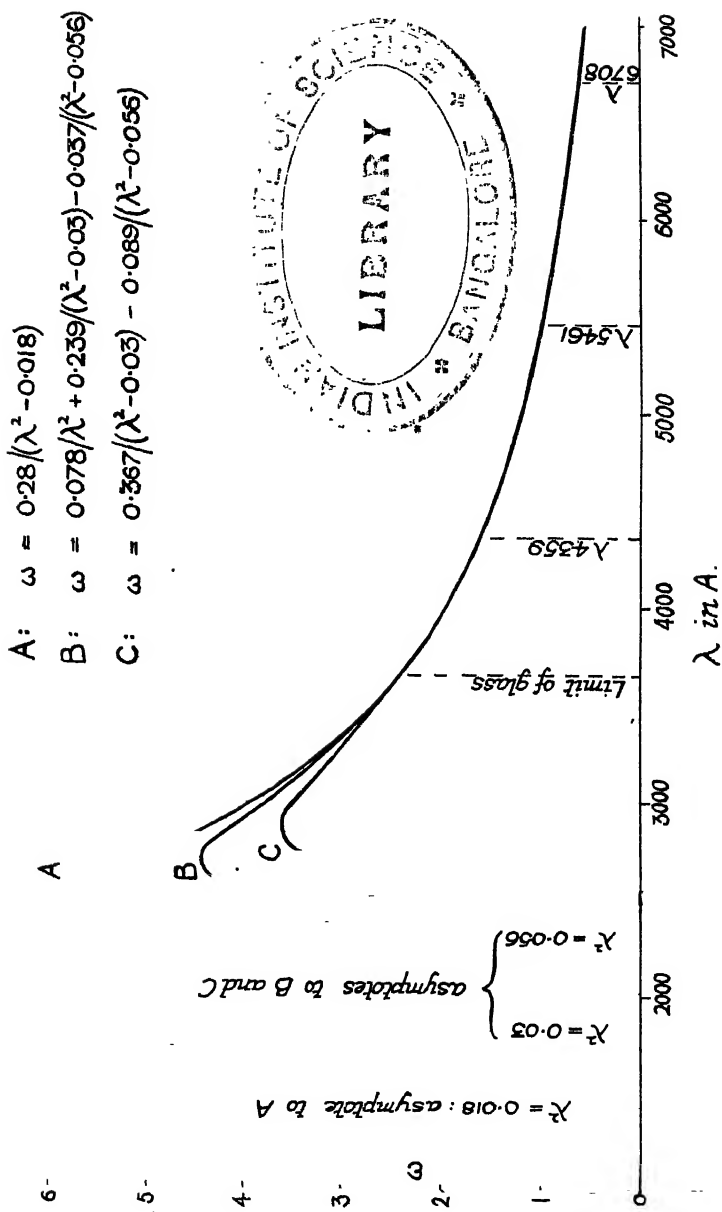
λ in A.

XV.

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